Transcript of Proceedings

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

GODDARD SPACE FLIGHT CENTER

1972 GSFC BATTERY WORKSHOP

FIRST DAY

Greenbelt, Maryland

Tuesday, 14 November 1972

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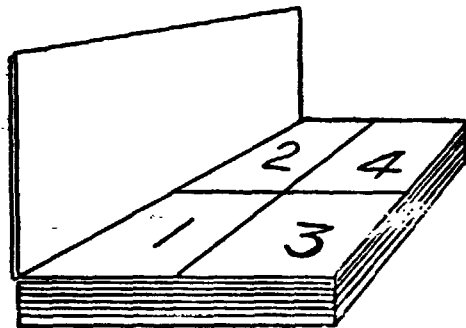
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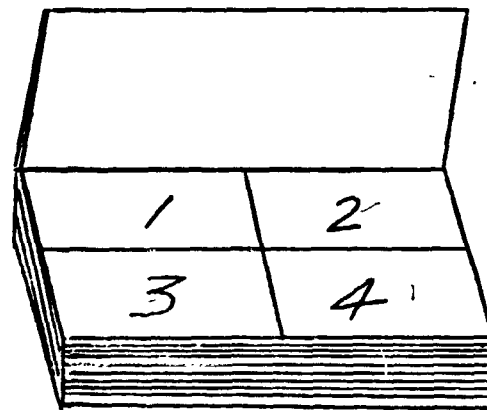
Gerald Halpert,
Workshop Chairman

N O T E

IN GENERAL THERE ARE FOUR SLIDES PER PAGE.   THE SLIDE

SEQUENCE IS THE FOLLOWING, REGARDLESS OF BOOK ORIENTATION.

(Vertical)

FIGURE NO. 1

(Horizontal)

FIGURE NO. 2

C O N T E N T S

FIRST DAY

Morning Session (Chairman: Hennigan)

Separators:

Afternoon Session (Chairman: Halpert)

Materials and Processing

LIST OF FIGURES

P R O C E E D I N G S

HALPERT: Welcome to Goddard Space Flight Center and the 1972 NASA/Goddard Battery Workshop. A full two-day program is planned for you including a session on separators, one on materials and processes, a third on storage and battery operation experience and finally a session on the improved energy density systems, namely, the nickel/hydrogen and silver/hydrogen systems. Plans call for each session to be a half day, however, it will not be restricted to that time. As in the past we welcome active audience participation. Although papers are prepared, your comments are solicited on any of the subjects.

I would offer a special welcome to our many vistors from Canada and France. We are happy to have you with us again.

This year we have some surprises, namely, two questionnaires on storage and use of the GSFC Moedel Specification (S-761-P-6). We request your participation in both of these surveys in order to best aid the manufacturer and user. The results will appear in the proceedings.

Tom Hennigan will chair the first session on separators in which some of the manufacturers will discuss their ideas. I will be chairman of the second session on materials and processes. Floyd Ford will be chairman of the Wednesday morning session on storage and application and Jim Dunlop, of Comsat, wi-1 be the improved energy density session chairman. If you plan to give a paper in any of the four sessions, please contact your chairman. I will be happy to answer any other questions. We hope the meeting will prove interesting and informative.

At this time we will start the 1972 workshop. A special guest is with us today to present the management viewpoint of the present and future for the space power industry, GSFC and NASA.

I would like to present Mr. Robert F. Baumann, Acting Assistant Director for Project Support - Space Applications and Technology Directorate, is representing our organization, the management of our organization, and has some words to say to us with regard to batteries and their use in space flight and what the future holds.

I would like to present at this time, Mr. Robert F. Baumann.

BAUMANN: Thank you, Jerry.

I would like to welcome you to the Goddard Space Flight Center. I would like to welcome you to the Goddard Space Flight Center's 1972 Battery Workshop.

Yesterday morning, at about 9:30, my counter Assistant Director at Space Applications and Technology said, "I have the delightful duty of opening the Battery Workshop tomorrow, but I am not going to be there, so how about you opening it for me?"

Well, my experience with batteries, up until that point in time was I go to the store and get them and put them in my flashlights and in my portable radios, and my depth sounder, and so forth, and I have just taken the battery as a tool, I have taken it for granted. I have felt, you know, the battery is there and you use it and that's about it.

So I started talking to Jerry to find out really what was going on in the nickel cadmium field, and what this meeting was all about. So, if I make any technical errors or any brash statements this morning, I hope you will forgive me.

Now, as most of you are aware, this workshop has been held each year for the past few years for the purpose of improving and accelerating the communication between government, industry, and the user communities.

It is my understanding that these meetings have become the annual focal point for the exchange of current nickel cadmium battery technology.

This meeting also affords an opportunity for each of you to look into the future in this field. In the past you have been responsible for taking an infant technology and developing it into a sophisticated space flight use, as well as expanding the general commercial applications.

The maintenance-free characteristics of the nickel cadmium battery make them especially suitable for use in space flight as a reliable power source and for use in numerous day-to-day items, such as electric shavers, pocket calculators, portable radios and TVs, hedge clippers, photoflash units, electric toothbrushes, and walkie-talkies.

For the immediate future in this field, NASA is interested in several new developments in the nickel cadmium battery technology.

We are interested in developing a long-life, say, five-to-ten year battery system that can be operated reliably in space, with a depth of discharge between 40 to 60 percent.

You have made it possible in the past few years to not only increase the in-orbit life of the nickel cadmium cells, but to significantly increase the depth of discharge over a few years ago.

NASA is counting on you as a team for the next order of improvement in this area.

Now, in concert with the development of the long-life battery system, NASA, the Air Force, and the Navy, are interested in developing battery test technology which will enable accelerated life testing.

We would like to be able to reliably predict our battery system's operation for ten years in advance, based upon an accelerated life test of only four to forty days.

This is, indeed, a great challenge.

Several years ago, we produced an interim model specification for high reliability nickel cadmium cells. This specification admittedly used a shotgun approach, which may have required inefficient testing and quality control provisions not currently needed to produce highly reliable cells.

We are currently evaluating this document and running tests to establish the relative importance of the different specified requirements, with a view of producing perhaps a more reasonable specification, which should result in lower cost product, easier to manufacture and test.

This effort, again, uses the combined talents of the government, university, and industry team.

Another area of interest for the future is to extend the cell capacity from the present state of the art of approximately 100 ampere hours to 200 ampere hours.

This larger capacity cell could possibly be used in the space station application and represents a technological challenge for the future.

I was requested to briefly talk to the project viewpoint versus the technological viewpoint of battery development.

The project is interested in an integrated power system, one of the elements of which is an energy storage device, usually a battery.

They want the system to be infinitely reliable, weigh nothing, take no space, provide an infinite number of voltages, provide infinite regulation, survive bitter cold and extreme heat, be produced on a tight schedule, and cost nothing.

The technologist, on the other hand, looks at these requirements as an opportunity to conduct extended research in power conversion and control, materials, chemistry, electrochemistry, manufacturing techniques, and life testing.

As you know, this is a bit of an exaggeration, but it serves to illustrate where the two parties start the negotiations from which a reliable power system is generated, and you are the people that see to it that a critical element of this system is provided, reliable nickel cadmium cells.

For that, we thank you.

I wish you a productive and highly successful meeting, and thank you for your kind attention.

(Applause.)

HALPERT: I thank Mr. Baumann for his very intert-
ing and stimulating talk, and he does show us, as he says,
where negotiations start and that we have some work to do.

We will now start our first session. Our chairman
is Tom Hennigan. The subject is separator materials. Tom
Hennigan has been involved with nickel cadmium battery develop-
ment for many years. He has in recent years coordinated the
separator studies and new developments. As a member of the
space power technology team, it gives me great pleasure to
introduce Tom Hennigan.

HENNIGAN: Thank you.

I would also like to welcome to our meeting this
morning -- and I would like to move along fairly quick here --
I have the list of speakers that we are going to try to go
through this morning, and I would like to just read them off,
so the people that are going to speak, or said they would
speak, know what order they are in. We don't print programs
for these things.

Of course, I will be the first to talk; then,
Aaron Fisher of Goddard; and Harvey Seiger of Heliotek;
then Earl Carr, E.P.; Rampel, General Electric; Willard
Scott of TRW; Stephenson of Motorola; and Jim Dunlop of COMSAT.

I don't know if we will cover all these this
morning, but we will give it a go.

For the next 15 minutes or so, I would like to
cover the data and information resulting from the continu-
ation of the NICAD separator tests that have been reported
on for the last two workshops.

As discussed previously, nonwoven nylons and
polypropylenes were selected on a Goddard contract, and
these were selected at the ESB Technology Laboratories.

These materials were given to Eagle-Picher for
fabrication of sealed 6 ampere per hour NICAD cells, and
these cells have been cycled for a year, or approximately
6000 cycles at the Naval Ammunition Depot in Crane, and
they have completed the 6000 a couple of months ago.

At the same time, we are giving these materials, both the virgin materials and tl ʼ cycled materials to the Bureau of Standards to c' aracterize the materials, new and as used, so we can see i. we can determine what degradation mechanisms and changes in characteristics take place during the cycle program.

Most of the cylcling was done at 20 ʋegrees centigrade and at 25 percent depth of discharge in a 90-minute orbit.

Except for the initial few hundred cycles, the recharge was limited to 103 to 110 percent.

(Slide 1.)

In the first viewgraph, here are six of the materials that we have been testing for the 6000 cycles.

Now, in addition to these materials, if you remember, we reported last year there were three other materials that we had selected as the type of materials that were likely to fail in the cell, and all those materials failed before 1000 cycles.

Now, on this slide, here we have the pack number, which identifies the pack at Crane's, and the material types are listed.

Pellon 2505 is the more or less standard nylon that is used in cells. It was referred to as 2505- ML before.

On the Pellon, 2505-K4 is calendared material which was as received. "AR" means "as received."

"W" means it was treated.

The third one is Pellon 2505-K4, which was washed in dilute hydrochloric acid.

In the polypropylenes, we have the GAF WEX-1242, which was washed in methanol. The GAF, same material, which is cycled as received.

A Hercules material, which was a microfiber type of material, which was used as received, and a

Pellon polypropylene, which is FT-2140.

Now, during the test program, and approximately every 1500 cycles, one of the cells was taken out. We started with 6 cells in most cases, and the cells were taken apart and analyzed for the following:

The amount of electrolyte that they would hold, and the amount of hydroxide and carbonate in the material.

Four separators were removed from each cell, two from the center of the pack and two from near the outside of the pack.

The next two slides have the results of the analysis of the amount of electrolyte retention.

(Slide 2.)

Now, here we have retention. Retention on the left there in grams per centimeter cubed, and the cycle life on the bottom.

Now, we only ran these 6000 cycles, if you remember.

So the top line is the 2505 star , nylon and the bottom line is the 2505 -- that should id K4W -- I didn't put the 2505-K4 as received up there.

The points are a little scattered on that one, but they seem to fall right -- three of them fell very close to the bottom line.

And as you can see, we are losing some of the electrolyte, as we cycle the cells, and I did extrapolate those lines out, and just kind of an opinion, it looks like you can sort of predict when these cells may fail.

I did go through a lot of data from the last 10 years of cells that were cycled under this type of regime, and they normally fail between 10,000 and 15,000 cycles, in other words, one to two years.

Now, the capacities on these cells, after the 6000 cycles, were -- there were only two cells left in each group 6, 6.2, and 6.1, and 6.6 ah.

Can I have the next slide, Jerry?

(Slide 3.)

These are the polypropylene materials, and again we have the same X and Y axis, and the top line, with the triangles, is the Hercules material, which has a similar curve as the nylon.

All the rest of the polypropylenes fell between these two dotted lines, which you see in the left-hand corner.

Now, I don't know if we plan --- if they are extrapolating that one out like we did the other one.

There is some opinion which I will express later by the Hercules people, what's going on in this material.

Now, the capaciti₁ of the Hercules material was as shown here, they were all greater than 6. The wash material of GAF was somewhat scattered, and some were low.

The as received material GAF was at least all staying together, and the Pelbn material, polypropylene, was somewhat scattered and lower than six.

By the way, these capacities are to -- in both slides -- are to 115 volts.

If I gave you the data, on most of these cells, to half a volt, we would pretty much get over 6 ampere hours on most cells, except for some of these very low ones here.

Now, I want that photograph.

Unfortunately, last night I found one of my slides was missing. It was too late to do anything about it this morning.

Now, during the course of the tests, we took the materials out, of course, these patches, we will call them, that we took out from the center and the side -- the outer extremes of the cell -- and we looked at them and photographed them. That's about all we have done so far.

Even with that sir~le little thing, we see some very interesting resul ₃ coming out of these materials.

(Slide 4.)

I don't know if you are all going to be able to see these too well, but after -- sometime today I will set up the photograph someplace around the room here, and you can look at them a little closer, if you would like to.

Now, this is the separator material from -- after 4500 cycles, for nylon, the negative side, in other words, the side facing the negative electrode. And the material numbers are called out here, the 2505s, with their various treatments or calendaring, and so forth.

You will notice that the two in the center are from the center plates, and the extreme ones are from the outside plates.

During the discussion, I will call this material cadmium. We are not sure just what it is. We haven't had a chance to do any analysis on it yet, whether it is cadmium or a compound of cadmium or if there is some nickel compounds in there also.

Is Floyd back there? He has got some slides.

VOICE: I have got one of them here.

HENNIGAN: Okay.

(Slide 5.)

HENNIGAN: Can you put the lights out back there?

This is the nylon material on the positive side, in other words, the side facing the positive.

Now, these are the same pieces that you saw in the last slide, just turned over. Now, actually, in these slides, and even in the photographs, the -- that side looks much darker than it really is.

Could I have the next slide, please.

(Slide 6.)

FIGURE 1

PACK NO.	MATERIAL TYPE	MANUFACTURER & STYLE NO.	MODIFIED OR AS RECEIVED
2E	NYLON	PELLON, 2505*	AR
46C	"	PELLON, 2505 K4	AR
49B	"	PELLON, 2505 K4	W
22C	POLYPROPYLENE	GAF, WEX 1242	W
38F	"	GAF, WEX 1242	AR
25D	"	HERC, 2665-15	AR
31C	"	PELLON, FT 2140	AR

*WAS 2505 ML

NYLON
(NON-WOVEN)

CAPACITIES AFTER 6000 CYCLES

△ 6.0 – 6.2
□ 6.1 – 6.6

2505
2505■ K4W

ELECTROLYTE RETENTION gm/cm³
0.7 0.6 0.5 0.4 0.3 0.2 0.1 0

CYCLES
1500 3000 4500 6000 9000 12000 15000
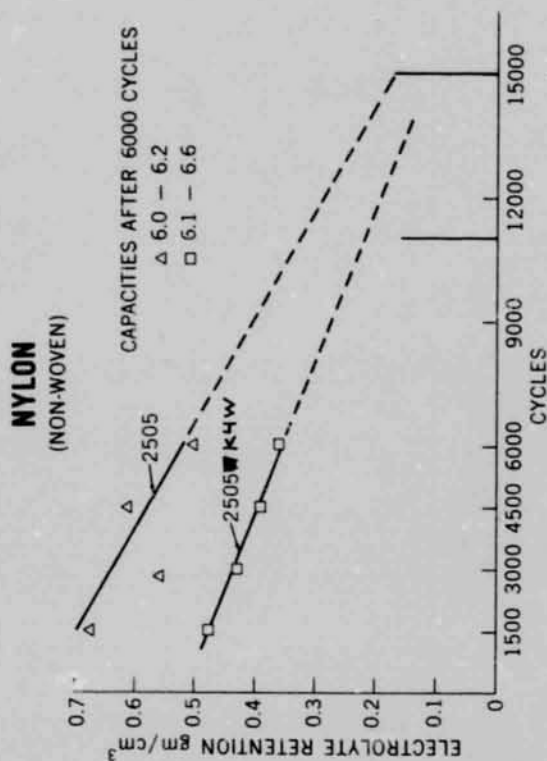
FIGURE 2

POLYPROPYLENE
(NON-WOVEN)

CAPACITIES OF CELLS AFTER 6000 CYCLES

PACK NO.	CAPACITIES (AH)
25D (HERC)	6.0,6.5,6.6,6.8,6.8
22C (WEX 1242 W)	1.8,2.8,5.3
38F (WEX 1242 AR)	4.3,4.6,4.8
31C (FT 2140 AR)	2.3,4.8,5.3

ELECTROLYTE RETENTION gm/cm³
0.7 0.6 0.5 0.4 0.3 0.2 0.1 0

CYCLES
1500 3000 4500 6000 9000 12000 15000
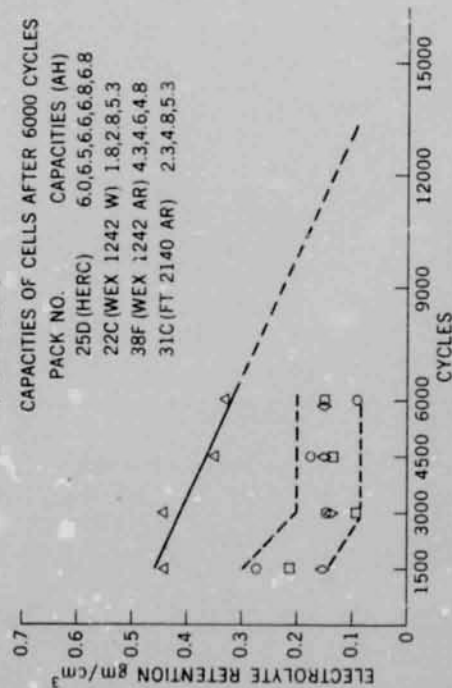
FIGURE 3

FIGURE 4

HENNIGAN: Now, this is the polypropylene materials, with the negative side showing, and again we have the center parts in the middle and the outside parts on the outside, and as you see there, they are listed down there on the left-hand side, what materials they are.

And you will notice most of the materials are quite dark, and the Hercules material is kind of not too uniform in the shade of darkness.

Now, if you would kind of keep your attention on these two right here,I would like to bring up something to you in the next slide that seems rather significant.

(Slide 7.)

This is the positive side, now, the same materials, that you looked at in the last slide, turned over, and you will see here that the top one, the cadmium has gone right through and the Hercules, there it is a kind of a grayish color, but it hasn't gone through.

Now, in this one here, which I pointed out last time, it hasn't gone through these two, but it did go through the extremes.

Now, one of the things that showed up there is the ones in the middle, Samples 10 nd 11, were very dry, they had about one tenth the amount of electrolyte that these had (indicating). So, if there is no electrolyte in the separator, or essentially none, the cadmium can't migrate and it seems from this information that if there is a lot of electrolyte, it only goes through partway, but if it is down in that lower end of the retention curve, say around a tenth to two tenths gram per centimeter cube, the cadmium will migrate through.

That's all for that slide.

I need the viewgraph again, though. Wait a minute, I have got one more slide.

(Slide 8.)

Now, you are going to have to believe me on this one.
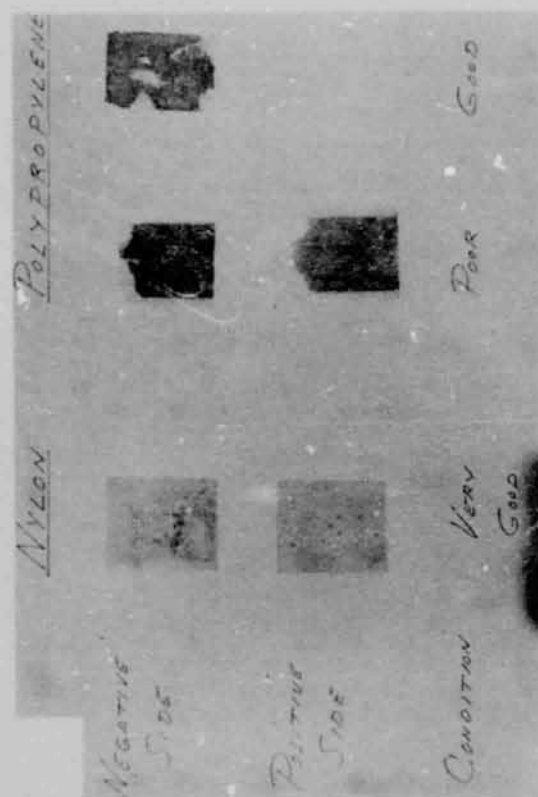
FIGURE 6

FIGURE 8

FIGURE 5

FIGURE 7

10A

This is a 6000 cycles, and I took some of the various materials, the nylons, and here's two polypropylenes, and as you can see on the negative side is a little bit of cadmium, and on the positive side on the nylon there is none.

On this polypropylene here, which is one of the microfibers, the material has gone right through.

This is the Hercules material here, and you probably can't even see it. In fact, I didn't think it was on the slide when I looked at it, but it is almost pure white, so it did not go through the Hercules material, and I kind of gave them a rating as to what I thought about them, mainly, Hercules, I didn't give them a very good because there was quite a bit on the negative side, but it didn't seem to be bothering the cell.

Okay. Then that is the 6000 cycles, and they all look -- that was typical of the group.

May I have the viewgraph?

(Slides 9&10.)

Now, I am going to go through these kind of quickly, because I don't want to take up too much time here, but what we have here is the analysis during cycling of the various materials for hydroxide and carbonate.

Hydroxide is on your left; carbonate is on your right.

And we start at the top with the standard nylon and the other two types of nylon are the two bottom ones.

And I am kind of surprised they stay so -- they seem to stay so constant over the cycle life, and I will show you the same information in the next viewgraph on the polypropylenes.

These here, if you can use your imagination a little bit on some of them, they don't change too much, and they also seem to stay constant.

Well, I would just like to express an opinion, not a conclusion, on these slides, that maybe what we are losing is the water only, during the cycling program.

Let's see, may I have the next one, please.

(Slide 11.)

Now, after the test program was all over,
we had a few cells left of each group, and we wanted to
determine whether these cells were shorted.

I mean, when you take them apart, the certainly
look like they are, especially some of the polypropylenes.

So we tried some various short tests, but didn't
seem to show up anything.

So we did this test: Charge a cell for, oh,
about five minutes, I forget the rate off-hand, and just
let them sit on open circuit for a long time.

Now the data we have here is after two months
on open circuit voltage, to see if they will maintain
over one volt. And as you see, one of the nylons, the
standard nylons, failed, it was below a volt, I don't
know if you would call that a failure; where two of them
have stayed up over a volt.

And in the polypropylenes, the Hercules
material has stayed over a volt for two months, and
the rest of them have gone down to essentially zero.

Now, the four that are up there, that show
cells below one volt, went down one to two weeks after
we started the test. The others have been holding up
there for some time.

So, from all these tests we have had, I would
just like to express an opinion. I don't know if we
can really prove all these, but --

Now, the cadmium migration -- is this on?

Oh, yes.

The cadmium migration through the separator
appears to be retarded if the separator retains a
large amount of electrolyte, and, of course, this tends
to slow down the shorting mechanism.

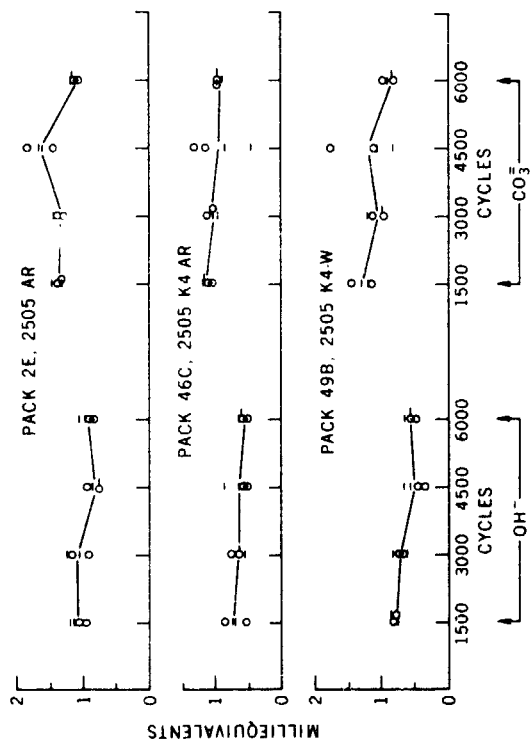This is strictly an opinion: the reason nylon

FIGURE 10

FIGURE 9

DECAY OF CELL OPEN CIRCUIT VOLTAGE

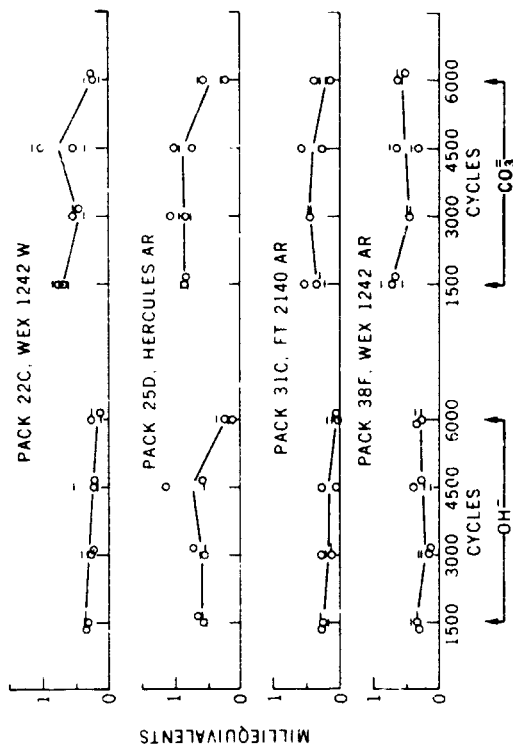| Material	number of cells	Cells Below 1.0 volts	
2505	1	1	
2505K4 AR	2	0	} Nylons
2505K4 W	2	0	
Hercules	1	0	
wex1242 W	2	1	} Polypropylenes
WEX1242 AR	2	1	
FT2140 AR	2	1	

FIGURE 11

12A

·retains quite a bit of electrolyte is that the lubricant is probably not very stable; however, the surface of the nylon degrades and thus wetting in the material remains at a high value.

A water loss may be -- could be the mechanism of the separator drying out, water loss only, and nylon, under conditions similar to the test, seems still to be a good separator to use for two to three years in a satellite operation, certainly good for many of the missions that we only have one year design life on.

I would like to acknowledge the help of a lot of people in this program, especially the personnel at . NAD Crane,., which I think did a terrific job in this particular program.

One of the main tasks of this whole thing was trying to get those separators intact, and, of course, I feel they did a very careful analysis along the way.

So I thank you, and if you have any questions, I will try to answer them.

(Applause.)

HENNIGAN: So our next speaker.will be somewhat of a continuation of the materials, the results of the materials that we had, as far as the characteristics of the materials before cycling and, I think we have some of the characteristics after the 6000 cycles, or after the various cycle bits.

We did have a question back there. Guy?

RAMPEL: Yes, Guy Rampel, General Electric.

Grams per centimeter cubed for electrolyte retention. Where did you get the thickness dimension, before the separator was in the cell, or afterwards?

HENNIGAN: No, that is after it was dried out. We take the separator and leech out the electrolyte that is in the separator patch, okay? And then it is titrated, and then we take the separator out and dry it.

Now, that's the thickness dimension we got after it was dried out.

RAMPEL: Thank you.

HENNIGAN: Boh?

STEINHAUER: Bob Steinhauer, Hughes. ...

Tom, two things: one, you had some little marks on the chemical charts, parallel or horizontal marks,

What did those mean?

HENNIGAN: Oh, those were maximum/minimums.

Is that what you mean?

STEINHAUER: Yes, but some of the marks, there were points outside of those two marks.

HENNIGAN: Maybe I plotted all the points. I think I did.

There are four values there, okay? There are four values on each separator, so I think I plotted them all.

STEINHAUER: Okay.

HENNIGAN: Okay.

STEINHAUER: Second, this is essentially a low earth orbit testing.

HENNIGAN: Right.

STEINHAUER: I am very concerned with whether that type of data is extrapable to synchronous orbit testing, and if you people have any plans to run tests more in a synchronous orbit?

HENNIGAN: Well, I don't know if you can extrapolate it That is always a hard question to answer.

But we have put some of the 2505 type separator cells on continous overcharge at C/30, and we intend to take these cells out once every three months. We only have three cells, so we can go nine months with that one. So we will see if that correlates with drying out also,

and those cells have been on about a month.

I do intend maybe to take the cells we got left over from the first program and also continuously trickle charge those and see how they operate.

BELOVE: Tom?

HENNIGAN: Yes.

BELOVE: Belove, Marathon.

HENNIGAN: Oh, yes, sir.

BELOVE: Tom, how do you relate the condition of the separator to the plates themselves? You show separator with -- in various conditions of having more or less material on them, but did anyone examine the plates to see whether the plates themselves were full?

What is the relationship between the two?

HENNIGAN: Well, we saved all the cell stacks after they were put through a   soxhlet   and washed out, so we have all those materials available to us, it is just that we have got to get the time to sit down and see what we want to do with them and what kind of measurements we want to make.

BELOVE: I have one other question.

Did I hear you correctly to say that the wetter the separator, the less material appeared to be -- appeared on the separator?

HENNIGAN: Appeared to migrate through it.

BELOVE: To migrate through. That is strange, isn't it? It would appear as though the wetter the separator, the more tendency for material to migrate through.

HENNIGAN: Well, if you have got any opinions on it, I -- we would like to hear it. I don't know why it happens.

BELOVE: Yes.

HENNIGAN: We have another question.

GRIFFIN: Mallory Battery (Canada).

I would like to ask you what you think about the electrode gap here when you start designing these cells, I notice you have different dry thicknesses on all these materials.

Could you comment on how many layers you put in, or whether it is just one layer, and also what you think about these materials. Are these production materials, are they lab tests, pilot tests, what?

HENNIGAN: Well, to answer one question, there is only layer involved in each -- between the positive and negative. It is put in in a U-fold type of assembly.

Most of the materials -- well, the Pellon material, I would say it is a production material. The GAF is, what would you call that, a semi-pilot plant, pilot plant type operation. And Hercules is a pilot plant operation. They are not made out of a beaker, they all have some type of a machine comb(?) with them. The Hercules one is kind of a standard machine that is used in making micro-fibers.

GRIFFIN: Well, if you are going to use just one electrode gap with these different thicknesses, have you thought of altering the electrode gap to fit the absorber system rather than t. ing to make the absorber system fit the electrode system?

MR. HENNIGAN: Well, we are going ahead with some more tests, and one of them here is a variation of density of material, which, the Hercules people can vary the density to whatever you would like, and we are going to try maybe three densities.

I don't know what the thickness of these materials are, but I would expect as the density goes down, they are a little bit thinner, but I don't have any numbers.

Mr. Lyons, is that right?

LYONS: Lyons, Howard Textile. (voice low volume)

How does the denier of the fiber of one compared with the other affect the amount of retention of the electrolyte or the deposit?

HENNIGAN: I don't feel I could answer that question.

The next speaker is going to talk about some of the characteristics.

Now, I don't know if that is included or not. But why don't we bring him on, if you are interested in the characteristics.

Do I see another hand?

Joel?

BACHER: Bacher, RCA.

Tom, you expressed an opinion on the usability of the nylon samples for one and two year missions. I didn't catch a summary on the polypropylene materials, or your opinion on the suitability.

HENNIGAN: Well, I guess you have to -- if you want a five to ten year battery at zero to 25 degrees C, and especially the higher temperature, I think the consensus is you have to go to some other material than nylon, and polypropylene seems to be a good bet.

BACHER: But does it show -- do you think it showed a marked improvement in retarging migration?

HENNIGAN: Only the Hercules. It was comparable to the nylon.

There is one other thing I would like to say about the whole program. The only material that was comparable to nylon electrically, as far as charge voltages -- well, discharge didn't make a whole lot of difference, but charge, was the Hercules material. It is about the only material we tested that we could say was a substitute for nylon today.

However, I don't see any sense in substituting if you have got a short mission.

BACHER: Thank you.

HENNIGAN: Any other questions? (Additional information on page 71.)
We will bring on the next speaker, who has some data on the characteristics of these materials

before cycling, and some information after cycling.

This is Aaron Fisher, who is at the Materials Branch at Goddard Space Flight Center.

FISHER: First off, I want to thank Tom for the very fine description he gave of the various types of tests, at least from the Crane point of view, the Crane angle, the electricals.

What we are trying to do is portray a depth type of physical property description and tie that in with some of the properties that were ongoing in the batteries as they were brought out for the 1500, 3000, 4500, and 6000 cycles.

I want to say that the Bureau of Standards has been doing practically all of our work in regard to the particular properties we are going to talk about, and we have prepared for you a preliminary interim report, which eveyone is going to have a copy of, that is, whoever wants one. And within it, we have the particular techniques that are being used, and the description of them.

Basically, they are out of the pages of "Screening Methods of Fleisher and Cooper." So, if you note particular captions on some of these columns, the techniques for obtaining these particular data are as described in the set of interim data from NBS, previously noted.

Now, I have been sort of forewarned that "please do not throw too much data at the people," but it is something I think that we may have to live with, at least for now, because it is the only way that one can look at all of the parameters and at battery conditions at the same time, and even though it may look voluminous, maybe we can get something out of it.

So, let me put this particular viewgraph on.

(Slide 12).

As you see here, we have essentially the same materials that Tom has spoken about before. The 2505 that is; the ML-2505 Pellon K4 calendared.

The next one is the calendared Pellon K4 with the hydrochloric acid treatment, .7% treatment.

PROPERTIES OF BATTERY SEPARATOR MATERIALS RELATED TO ELECTRICALS OF CYCLED NI-CAD CELLS USING THEM.

BATTERY SEPARATOR MATERIAL	APPARENT DENSITY gm/cm³	THICK in	31% KOH ABSORB gm/cm³	31% KOH ABSORB EXTR MAT'L gm/cm³	APPARENT POROSITY %	AIR PERM sec/300cc	WET OUT SECS	WET OUT EXTR MAT'L SECS	SPEC RESIST ohm cm	SPEC RESIST EXTR MAT'L ohm cm	KOH RETEN ON SEPAR gm/cm³ 15 30 45 60 x10² CYCLES	AVER PACK CAP ORIG 15 30 45 60 x10² CYCLES	AVER PACK RESIST x10³ ORIG 15 30 45 60 x10² CYCLES	CC KOH IN TEST CELL
A - PEL 2505 K4 C4 NYLON	0.317	0.0074	1.342	1.122	103	5.9	189	227	3.49	2.88	48-60 / 35-43	7.56-7.52-7.5 / 7.6-7.28	2.50-2.48 / 2.46-1.88 / 3.07	26
B - PEL 2505 K4 C4 7% HCL NEUT DRY 50°C NYLON	0.278	0.0082	1.331	1.172	102	3.9	314	864	3.33	3.49	48-43 / 39-37	7.69-7.58 / 7.63-7.08 / 7.16	5.77-3.6 / 2.58-2.6 / 4.0	26
I - PEL 2505 ML NYLON	0.173	0.0123	1.350	1.220	103	2.2	216	11	1.93	2.06	66-54 / 62-54	7.69-6.53 / 6.46-6.57 / 7.27	3.22-3.18 / 2.15-2.7 / 3.35	26
C - PEL FT 2140 POLYPROPYLENE	0.353	0.0084	0.937	0.894	71	8.5	1506	9900	5.46	5.67	15-14 / 15-15	-7.35 / 7.06-7.54 / 6.34	6.55-5.32 / 7.12-9.07 / 10.13	24
D - HER RT 37 2005 15 MICRO POLYPROPYLENE	0.193	0.0090	2.060	—	158	84.6	15	9900	2.20	—	44-45 / 35-30 / 33	7.06-7.82 / 7.54-7.47 / 7.23	31-2.59 / 3.63-3.66 / 4.08	27
H - GAF WEX 1242 304PO POLYPROPYLENE	0.242	0.0112	0.789	0.754	61	37	4	9900	7.44	3.67	21-09 / 14-15	7.67-6.78 / 6.30-6.30 / 6.50	2.92-2.27 / 5.32-4.83 / 6.73	24
J - GAF WEX 1242 304PO METH WASH + DRY POLYPROPYLENE	0.227	0.0094	0.886	0.820	58	27	<3600	9900	3.10	3.22	27-14 / 17-09	7.46 7.31 / 7.09 6.34 / 6.42	2.78-3.47 / 4.38-4.7 / 6.87	24
E - KEN E 1451 POLYPROPYLENE	0.600	0.0046	0.474	0.485	36	223.7	248	9900	30.20	28.50			23-99	21
F - KEN E 1451 POLYPROPYLENE METH WASH + DRY	0.644	0.0045	0.478	0.452	36	15-9	<3600	9300	26.75	28.27			8-12	21
G - KEN E 1451 POLYPROPYLENE + METH WASH + DRY - CONC H₂SO₄ + NEUT 90°C DRY	0.583	0.0049	0.684	0.433	53	148.2	<3600	9300	28.35	25.40			6-98	21

COMPANY MATERIALS: PELLON - HERCULES - GENERAL ANILINE & FILM - KENDALL

CELL CAPACITY VALUES DETERMINED BY DISCHARGE TO 0.5 VOLTS AT 3 AMPS

A. FISHER GODDARD SPACE FLIGHT CENTER MATERIALS ENGINEERING BRANCH CODE 764 DECEMBER 1972

FIGURE 12

The third one is the maximum loft type material, the 2505ML.

The next one is the Pellon 2140, which is the polypropylene.

The subsequent one is the Her.ules microfiber. And then the GAF material, WEXs, et cetera.

I will get around to bringing some of those up where we can see the data.

Now, we have these various columns and their titles, apparent density, percent KOH absorption, apparent porosity, permeabilities and from all of these, we would hope that we can come out with some of those parameters which indicate which particular separator might be a more desirable type.

Now, if you look in the apparent density column, we find that the polypropylene, that is, the microfiber polypropylene and the MLs ar⋅ sharing the position for very low apparent density, and this sort of ties in also with the proposition of absorption.

You are beginning to get the large amount of absorption in that area of low density, including also the K4 and the K4HCl treatment.

Now, the apparent porosity is a term that we get from taking the absorbed weight and density of the material and get a volume and compare that with the original volume of the separator.

So we can see that the apparent porosity of the material is high for the nylons and also for the microfiber polypropylene.

The other particular material, the WEX, the W-E-X material, and also the Kendell material, which is further on down below, have not shown up well in this particular area of porosity.

We have our air permeability, which is the time it takes for - in seconds - for 300 CC to pass through a separator. These values are for the particular Gurley type of instrumentation that was used.

Now the wet out in seconds is an operation which we sort of devised. It is a circular Lucite plate with variously increasing grooved diameters, and it has got a hole in the center.

What we do is drop some of the KOH material down through the hole, watch the expanding wetting KOH and see how far it expands in the particular period of time, as viewed against the grooved circles of increasing diameter.

Now, the wet out is an indication of how long it takes to actually disappear, so we can see that the low numbers over here in the seconds are indicative of a material which is going to wet out quite easily.

And from that point of view, we see that the initial K4 and the MLs and also the polypropylene, the microfiber polypropylene are very good in this particular regard.

The as received WEX 1242 also shows up quite well in this area.

The specific resistivity is as indicated in the Fleishman-Cooper screening technique. That is the particular method that we used here.

And we can see, as we are coming down the column, that .30, .20 density and two below those, those are the Kendall materials that have the high density, approximately .6 to start with, and we can see that the specific resistivities are quite high with the .6 density.

The other resistivities are nominal and the primary indication here is that with the high densities, we are getting the high resistivities, and otherwise, we have a nominal type of specific resistance.

The next column is the KOH retention on the separator, gram centimeters per cubic centimeter, and that is basically the same type of data that Tom presented before, except now we see it in the context of all the other particular properties that have gone before.

They are read left to right for the 1500 through 6000 cycles, and we can see that the retention is greatest, say, with the nylons, and with the polypropylene, the microfiber polypropylene, and that for the

others, the KOH retention is quite low, I mean, noticeably low, so that you can see there is quite an apparent difference between that group, and the micropolypropylene nylon group.

Now, the pack capacity is indicated in the next column, and that runs from an original value, before cycling, through 6000 cycles, so that the first number there, up on the top column is 7.56, that would be the original number. And 7.52, 7.5, 7.6, and 7.28 are progressive values as the cycles increase to 6000 cycles.

So we can see that the Pellon K4 material is holding up pretty well in regard to the capacity of the cell.

I want to also indicate that these capacity values are different from Tom's in that Tom's went down to, I believe, one and a quarter - was that it, Tom?

HENNIGAN: One one five.

FISHER: One one five volts (1.15V).

These go down to a half volt, so these numbers are higher than in Tom's data which were in the neighborhood of about six. These were taken from the same data, incidentally, but are an extension of it.

As we go along, we can see differences in the tapering off of the capacities, say, in those values which correspond with a KOH retention, that is quite low.

One of the unusual things that occurred in this particular operation was the capacities for the ML-2505, which we had been considering as sort of standard, being quite lower, appreciably lower than the K4 material. The uniformity of the Pellon K4 material, both in the KOH retention and the capacity is quite noticeable as compared to the 2505-ML, which might lead me to say that even though it is a K4 calendar, that it might be a more uniform type of material, and possibly it should be used as sort of a control rather than the Pellon 2505-ML in future types of operations.

(Slide 12)

If you can recall the particular materials that we have there, basically the K4 and -

(Discussion off the record)

FISHER: These are the actual cell resistivities in milliohms from the original on up through 6000 cycles again. These happen to be water colors, and I guess in the rain I may have wiped off some of them, but the numbers over there in the first column, we have about 2.46, I think that is the number, and one under it. 3.0'.

Basically, these follow the same type of procedure as on the previous column, that is, the first number is the original, and then they progress from left to right on out to 6000 milliohms.

We can see that as we get down into the area of the polypropylenes, where the retention on the separator is low, that we have resisitivi.y that is starting to climb.

If you compare the resistance here, the cell resistance here as compared with the one in the 2505-K4 calendar material, you see that the resistivity up here is comparatively low and that there is a general tendency for the resistance of the cell to move on up, possibly with the diminishing amount of KOH on the separator.

We really haven't probed into this particular area. This is practically brand-new data that I was looking at the other day, and we put it down for your information. We would like to present this and put it into the book so that you would be able to really look at it and possibly analyze it on your own.

What we have here, now, is a sort of in-depth type of view of what particular types of separators and their absorptivities, et cetera, and retentions, are doing in terms of the cell as it is progressing along through the 6000 cycles.

Originally, we thought that we were going to reflux our separator materials and get similar data to that before refluxing, refluxing with hot water. We were going to reflux them so that we could start with a standard which would compare with the material that we were going to get from Crane. Crane's materials was to have been or would be refluxed separator material from cycled batteries. So, we thought we would take our original materials and reflux them to see what kind of values we would get out of them in anticipation of what we would get from Crane.

Much to our surprise, we found that as we started looking at the polypropylenes, the properties that we thought we would be able to compare later, on battery c. cled and refluxed separators, disappeared because most of the polypropylenes had wetting agents or materials on them that dissolved in the soxhlet reflux action, so that - let me show you some of the indications of this.

(Discussion off the record)

FISHER: This is a wet out similar to the other wet out that we have up there in seconds.

This is after the material has been refluxed, and we see the 9900 seconds as an arbitrary number that we used to fit inot a computer schedule that we were doieng, but it actually means that it may never have gotten to the point where there was any kind of wetting out occurring, and you can see that with the polypropylene materials, including the microfiber material, that after refluxing the time for wet out increased tremendously, so that we had here a system which primarily, it would appear to me, had to depend upon, at least for wetting and absorption of electrolyte, had to depend upon the fact that there was a wetting agent material on the polypropylene.

However, as we look at the nylons, we see that although refluxing has occurred and some changes have occurred, that we are still able to get an absorption, or wetting out of the material.

Now, in the case of this number eleven, 11 seconds, I sort of investigated that on my own, and I could not believe that it had become so enhanced because of a refluxing operation, and we have been studying actual droplet form as it is affected by wetting, that is, we have a mirror arrangement under a microscope, and we can put a drop of - a known drop, a micrometer calibrated drop, on a fabric, - and take pictures of the way the drop is absorbed, and so we tought that maybe this very rapid absorption was possibly due to the fact that the nylon, when it was being measured, had not been thoroughly dried, and we did take pieces of nylon and subjected them to various drying cycles and it was apparent that those which were least dry showed the greatest tendency toward wetting, for whatever that might be, and as the nylon fabrics dried out, more and more, then the tendency for wetting decreased.

I might want to indicate that we are also involved in a study on the ability of KOH to wet various surfaces. This tool allows us to modify the surfaces of the fabrics. say, possibly with corona discharge or with oxidizing reagents, or possibly with wetting agents, and to quickly then be able to see in the microscope, on a time scale. just how rapidly the drops could be absorbed into the fabric as a function of the modifications on the particular material.

I have not brought any of the picutres, though we have hosts of them, blown up pictures, which show a lateral view of drops as they are disappearing into fabric materials, and maybe we can include some of those in the report that is going out.

That is about all I want to say for now.

(Applause)

FISHER: One further thing, these interim NBS reports will be available at lunch time. I will bring a batch of them up here, enough for everyone.

HENNIGAN: Do we have any questions for Mr. Fisher?

FISHER: I think on that question that arose before on the denier, I do not know whether you were talking about the denier, or whether it was really cross sectional area that you really had in mind.

It would appear to me that if you have a very fine fiber, and you do not have a wetting agent on it, you will have great difficulty with the microfiber in trying to wet it.

In fact, there were some operations that we could not get any data on at all, once the wetting agent was removed, but with the assistance of the wetting agent, nonwovens appear to be excellent absorbers of KOH solution, and I think some of those data might bear that out.

HENNIGAN: Are there any other questions for Mr. Fisher?

Bob Steinhauer?

STEINHAUER: Steinhauer, Hughes.

If that same wetting agent were used on a polypropylene with larger denier size or cross sectional area, would you expect similar results to the Hercules?

FISHER: If the same type of wetting - I did not get that, what was that again?

STEINHAUER: In other words, you attribute the properties - or at least, part of the properties of the Hercules material to that wetting agent.

What if some of the same wetting agent used on the Hercules material were applied to larger size fiber materials, would you expect the same results?

FISHER: No, not the same results.

I am saying that you would have a difference depending upon the thickness of cross sectional area of your fiber.

I am saying you can get very excellent results with a microfiber and a wetting agent. Without a wetting agent, no; you can take the same wetting agent and put it on another polypropylene material, yes, if it is the same type of denier or diameter, I would expect the same type of results.

If the fibers were of larger diameter, which means decreased surface area, I would expect a lesser type of result, i. e., absorption.

HENNIGAN: I would like to mention one thing about the wetting agent on the Hercules material, after these tests were over, we sent the material to Hercules, who offered, gratis, to analyze and see if they were losing it. Now that was a little difficult to analyze for because there isn't very much on there, plus the cadmium was interfering with their analysis, but it is their opinion that they lost some but it's leveled out.

Now, that is an opinion. I do not have any proof for it. But they did analyze the material for us before and after six thousand cycles.

Our next speaker this morning is Harvey Seiger from Heliotek and Harvey is going to explain

to us why some of these things are going on in the cell, like the drying out, is that right, Harvey? Electrolyte loss.

I want to make sure I have the right guy.

(Laughter.)

SEIGER: Harvey Seiger of Heliotek.

I don't think we will explain the whole thing, but I hope that we will start something towards understanding why one loses electrolyte from the separator and has it go into the electrodes.

I think it is pretty well established now at this redistribution does occur, and it appears in cells, regardless of the separator material that is used, although it is greater and it occurs apparently more rapidly with polypropylene than it does with the nylon.

Now one of the mechanisms that I have heard that has been postulated is that there is a corrosion of the grid.

We have considered it, but we are not going to treat it here because our consideration shows that it is not a prevailing mechanism.

Now, nylon degradation was not considered because redistribution occurred in cells with poly-propylene separators as well as those with nylon.

There are apparently two other mechanisms that occur in the cells, and one is simply a thickening of the positive electrode. Well, the entire cell as used is held under a mechanical constraint and if the positive electrode does thicken, it has got to exert its force on something, and the separator is compressable, so you are opening up additional volume in the positive electrode by its thickening, and you are compressing a wet separator, and you would simply squeeze the electrolyte out of the separator and then it could enter the positive electrode.

And I think that is all the time I am going to spend on that particular mechanism.

The second one that I believe prevails is the real objective of this presentation, and I contend, and I will try to establish some of it by some indirect evidence, that there is air entrapped in some of the voids, particularly of the negative electrodes at the time that the cells were sealed.

Now estimates are made of the amount of the air that is entrapped and it is surprisingly significant.

Now, as the cell is used, there is an exchange of the air with the electrolyte, from the separator, and you can visualize the competition between the separator and the electrodes for the electrolyte.

Now if the separator is hydrophobic, as with most polypropylenes, it won't fare well in this competition and the electrolyte can leave that separator and enter the voids in the electrodes.

Now, such a mechanism explains not only the electrolyte redistribution, which it is an ad hoc hypothesis, but it also helps explain some other phenomenon that we have known for some time.

And these are shown in my first figure.

(Slide 13.)

The first statement is merely an enunciation of the air entrapped mechanism in which there is an exchange. I shouldn't have used the word "diffused," it implies the mechanism.

There is an exchange between the separator and the electrodes.

Well, if you have air in the cell at the time it was sealed, you had nitrogen and oxygen, and so you will readily find that there is an amount of nitrogen in that cell, which I calculate to be on the order of 2, 2.5 psi in a 20 ampereohm cell.

Once we are equipped with this redistribution mechanism, and we see that the electrolyte is leaving the separator, we can explain some other things.

For instance, there was a cell that had been

designed not to explode, having a scavenger electrode,
it went out to Crane, and it did explode. Now we can
explain that.

Then the fourth item, is that there is a
sensitivity decrease of oxygen sensing electrodes,
which we can now assume, and I will try to establish
it during the presentation, that the loss of electrolyte
will inhibit -- or the loss of water will inhibit the
at which the signal electrode would operate, and that
would give rise to the loss of sensitivity.

And then the kinds of calculations that
we have gone through, the chemistry, help us to explain
why we observe on all the charge pressures a decreas
of steady state pressure as the state of charge of
the negatives is increased.

I am afraid that I won't be able to explain
all of it, but the calculations are very interesting
and it will show that there is a slight drying out.

And then once we do that, we can encounter
some data that Dennis Turner published in the Journal
of Electrochemical Technology in 1964, in which he had
a historesis and we can explain the historesis effect
on the basis of drying out.

And with that I would like to go into the
promulgation of the air entrapment mechanism.

That is enough of that slide. We will be
using it later.

Now historically, there has been a number of
methods for determining the amount of electrolyte to
add to a nickel cadmium cell, so that to have a
sufficient amount for the charge-discharge reactions,
and yet so much not to cause high pressures.

Now, one experimental method has been to add
incremental quantities of electrolyte and measure the
over-charge pressure and the capacity of the cells.

Now, I have a generalized set of curves
for the next one, which show this.

(Slide 14.)

We just add quanities of electrolyte to a cell
that we can enter, and plot the capacity on the dash

curve and the steady state pressures that we observe on the solid curve, and we do see that it is a sigmoid type curve.

I happen to remember for a 6 ampere hour cell, the first point correspondes to about 16 milliliters and the second bending upward, corresponds to about 18 milliliters; in a case like this, we would choose about 18 milliliters of electrolyte to add to a cell and that comes up again with the famous number of about 3 milliliters per ampere hour.

Now, in order to determine the amount of electrolyte to add to cells that we were making, we carried out a procedure such as this, and we determined that we needed about 65 milliliters of electrolyte, but we also determined very importantly that we did need about 4 ampere hours precharge in order to maximize the capacity, otherwise there was a limitation of capacity due to the positive electrode, in spite of the fact that we had some precharge in there.

If you carry out a precharge, it causes a dilution of the electrolyte.

Now, if one adds electrolyte to cells having discharged electrodes, and then you do the precharging by whatever method one choose, and then consider that cell again, when it is at a state of full charge and closed, the effect of precharging is always chemically the same. There is a dilution.

Now, in order to minimize this dilution, we decided to float the cell prior to the precharge, and later extract the excess electrolyte.

Now, if you follow this procedure, the amount of electrolyte that remains in the cell is now 78 milliliters.

The other procedure gave us 65, and now we have 78, and we have a measurement difference of 13 milliliters, that at this point, I want to suggest that that 13 milliliters of additional electrolyte has replaced air that was entrapped in the cell, when we did the original work.

And we might also suggest that the estimate

void volume in the separator and in the discharged
electrodes provides for us an interesting comparison.

May I have the second viewgraph, please.

(Slide 15.)

We proceeded to make a volume estimate of
unimpregnated voids in the electrodes and also in the
separator, and these particular cells, they have a total
void volume on the unimpregnated plaque of 113 cubic
centimeters; the void volume in the separator came out
to be 19.5 cubic centimeters, and the total therefore
was 132.

On impregnation, the positives had a
theoretical capacity based on weight gain of 25 ampere hours,
using the density of niclous hydroxide, we find a
residual void volume of -- we find that we have occupied
21 cubic centimeters.

Similarly for the negatives, we calculated
that we have impregnated 30 CCs of cadmium hydroxide,
and this gives us a total volume calculated in the
discharge state of 51 CCs, and the residual void volume,
therefore, is the difference between the total initial
voids and the volume of impregnated material, and it
comes out to be 81 CC, which is awfully close to the
78 that we actually put into the cell.

Now, we postulate that with the customary
filling of nickel cadmium cells with electrolyte, some
air is entrapped in the electrode, and as the cell is
used, this entrapped air is exchanged for electrolyte,
and this air enters the atmosphere of the cell.

Now, the source of the electrolyte for the
electrode is from the separator, resulting in a
diminished content in the separator.

Now, in the example given, if these cells were
filled in the customary manner, about 60 percent of the
electrolyte in the separator could migrate from the
separator to the electrodes.

Now similar calculations could be made for
any cell design, provided the plaque voids, loading
levels, and separator characteristics are determined.

AIR ENTRAPMENT MECHANISM

1. AIR ENTRAPPED IN ELECTRODES DIFFUSES OUT SLOWLY AND IS REPLACED BY ELECTROLYTE FROM THE SEPARATOR.

2. NITROGEN FOUND IN CELLS CAN BE EXPLAINED DIRECTLY FROM MECHANISM AND AMOUNT IS CALCULATED TO BE ABOUT 2.5 PSI IN 20 AH CELLS.

3. CELL WITH SCAVENGER ELECTRODE (Pt) EXPLODED AT NAD CRANE; CAN BE EXPLAINED ON BASIS OF AIR ENTRAPMENT.

4. SENSITIVITY DECREASE OF OXYGEN SENSING ELECTRODES WITH CYCLING CAN BE EXPLAINED ON BASIS OF DRYING OUT.

5. THE CONSIDERATIONS INVOLVED WITH THIS MECHANISM HELP EXPLAIN WHY THE OVERCHARGE PRESSURES DECREASE WITH INCREASING PRECHARGE OF THE NEGATIVE ELECTRODE.

6. THE AIR ENTRAPMENT MECHANISM HELPS EXPLAIN THE HYSTERESIS EFFECT IN TURNERS DATA ON PRESSURE DURING OVERCHARGE AS A FUNCTION OF STATE OF CHARGE OF THE NEGATIVE ELECTRODE.

FIGURE 13

VOID VOLUME ESTIMATE

VOID VOLUME OF UNIMPREGNATED PLAQUE   113 cm^3

VOID VOLUME OF SEPARATOR (RA1 P145 122, 50% VOIDS)   19 cm^3

TOTAL INITIAL VOIDS   132 cm^3

POSITIVE THEORETICAL CAPACITY 25 AH, VOLUME AT $\rho = 4.1$ g/cm^3 21 cm^3

NEGATIVE THEORETICAL CAPACITY 52 AH, VOLUME AT $\rho = 4.79$ g/cm^3 30 cm^3

VOLUME OF IMPREGNATED MATERIALS, DISCHARGED STATE   51 cm^3

RESIDUAL VOID VOLUME   81 cm^3

FIGURE 15
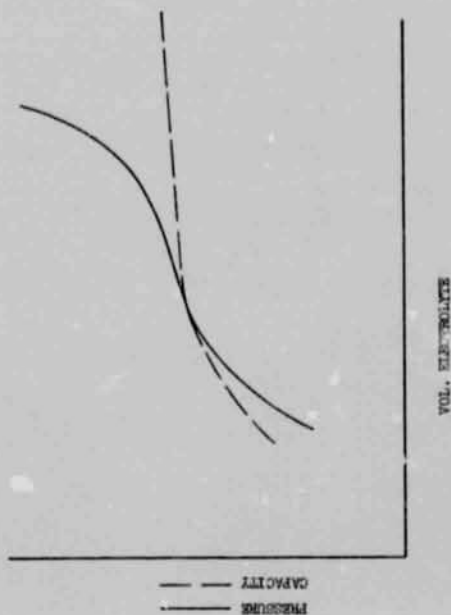
VOL. ELECTROLYTE

PRESSURE AND CAPACITY AS A FUNCTION OF ELECTROLYTE VOLUME

FIGURE 14

OXYGEN CONSUMING ELECTRODES
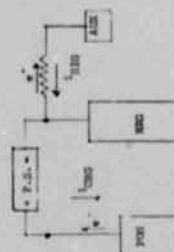
FIGURE 16

Now, since we have a postulate on air entrapment, and some preliminary evidence on it, as well as Tom Hennigan's experimental findings, this method can be used to probe some other questions and problems that exist pertaining to the nickel cadmium cells, and I would like to go on next to the nitrogen in the atmosphere of the cells.

Now, when the air leaves the electrodes, 20 percent is oxygen, which is consumed at the negative electrode, and the reamining 80 percent is nitrogen, which remains in the cell atmosphere. Now for the sake of simplicity in making calculations, the free space of a cell is taken as 80 cubic centimeters, and the quantity of nitrogen is four times ten to the minus four moles, resulting in a partial pressure of 2 psi.

Thus, if the cell is open and the composition of its atmosphere determined, nitrogen will be found.

Now, at the time of opening, should there be 5 psig in the cell, the volume composition would be 10 percent.

Now, I would like to go on to the four electrode cell explosion, and several years ago we had done some work on the inclusion of platinum catalyzed electrodes, in sealed nickel cadmium cells, to enhance recombination.

The purpose, to act as a scavenger, so that there would always be a signficant recombination reate for oxygen.

Now, during the development, we had realized that the amount of electrolyte that went into a cell had to be increased to avoid an explosively fast reaction at the fuel cell electrode, and this is particularly true at low temperatures, where hydrogen could be formed, and then the hydrogen-oxygen reaction would be explosive.

Now in subsequent testing of such cells at Crane, the worst happened. There was an explosion during a charge at low tempeature.

Now, if we use the air entrapment mechanism, and the electrolyte redistribution is applied, we can get a reasonable explanation for what went on there.

With the electrolyte redistribution, the amount

of electrolyte, about that platinum electrode, which was originally designed to be of considerable quantity, it decreased, and when the hydrogen formed during the charge at low temperature, and subsequently oxygen formed, they reacted violently, causing the explosion.

Now at this time we might speculate that if we were to redo this with platinum electrodes, they might be incorporated safely into the cells, providing that the entrapped air is removed first.

Let's talk now about the sensitivity decrease of oxygen sensing electrodes.

May I have the next slide, please?

(Slide 16.)

Oxygen sensing electrodes require water for operation.

I have drawn here a schematic of the three-electrode system.

We show a power supply on the top, charging the positive-negative electrodes, and we have an auxiliary electrode in there.

And the arrows show the direction of current. I like to use electrons so included as well as the usual standard designation for current.

Now, consider the cell, as it is just going into overcharge in which essentially all the nickelous hydroxide has been charged.

You now take hydroxyl ions, from which you get oxygen plus water.

At the negative electrode, you are still charging cadmium hydroxide to cadmium.

Now, the particular auxiliary electrode that I chose to take was the absorbed hydrogen mechanism. This could work equally well, if one wants to assume a peroxide mechanism.

What we show for the absorbed hydrogen mechanism

is that oxygen removes hydrogen that's absorbed on nickel sites on the negative electrode to form one.

That absorbed hydrogen is replaced by reaction two, in which water from the electrolyte is separated into hydroxyl plus the absorbed hydrogen.

At the negative electrode, which is the supply of the electrons in carrying out this reaction, at the negative electrode, we are discharging it in order to supply those electrons and hydroxyl that is used.

Well, very obviously, if you diminish the availability of water by either poor working or a diminished quantity of water that cannot get to the auxiliary electrode, then the signal will be decreased, and that will result in the loss of sensitivity.

Now, in a 1967 paper at the Power Sources Conference, the necessity of water transfer was noted.

And very interesting, on page 64 of the Power Sources Conferences, is the following information, and I quote it:

"These test cells, which were not hermetically sealed, appeared to dry out in about a thousand cycles."

These cells had been cycled at 50 percent depth of discharge, in about 1000 cycles, the performance degraded, and there was a loss of sensitivity of the signal electrode.

The addition of water, or electrolyte, restores the cycling ability and the anhydrous sensitivity.

So we have a case here where water was added to the cell that apparently had dried out and we were able to restore the sensitivity of the oxygen signal electrode.

Now, it may be concluded that the loss of a signal electrode sensitivity is due to interference with reaction 2 on this slide, which is,in turn,explained by the electrolyte redistribution.

The corollary that these auxiliary electrodes may have a more stable sensitivity while cycling is expected if one were first to take care of electrolyte

redistribution.

That   enough for that slide.

The next area doesn't bear directly. It is
going to make some contribution to the understanding of
some data that was publsihed in 1964 by Dennis Turner,
and it deals with tae decrease of the pressure on overcharge,
with an increase of precharge.

And we want to just understand some of the things
going on in the cell.

Let's consider a fully charged nickel cadmium
cell that is equipped with a resealable vent.

May I have the next slide, please?

(Slide 17.)

Now, while in overcharge oxygen is generated
at the positive electrode, indicated by the first slide
and by the first equation.

And the negative electrode charges to an extent that
is equivalent to the number of moles present in the gaseous
state of the cell. When that oxygen is vented out, the
state of charge of the negative electrode again increases.

Now, if you consider all the changes that could
possibly occur in the cell, physical and chemical, in the
negative electrode, with the cadmium hydroxide, the mobile
volume of cadmium hydroxide is 30.6 cubic centimeters. The
mobile volume of cadmium is 13.0, and so the change in the
mobile volume is 17.6 cubic centimeters.

We are not only generating the water, as shown
in the next reaction, but we are diluting electrolyte, and
when you dilute electrolyte, inject water into 34 percent
KOH, it doesn't give you one milliliter volume change for
one gram.

We wanted to estimate what the possible mobile
volume of water would be when diluted into the electrolyte,
and so we went to the literature and we pulled out some
data for 34 percent and 33 percent electrolyte.

The compositions are indicated. We have taken one
liter in both cases. We now assume that we are going to

inject water into a 34 percent solution of KOH, so we start
off with the analytical value and we are going to make up
a hypothetical solution, 33 percent KOH and retain the same
mass, so this is constant, the mass of potassium hydroxide,
and the question is how much water must be added to this
to dilute.

And when we finish the calculation, we find
that there is a mass change of 40.5 grams and a volume
change of 38.7, so that the effective density of the
water, when going into dilution, is 1.04, and if we raise
this a little, we will find that the partial molal volume
of water is 17.3 cubic centimeters.

The point is that while we are generating 18
grams of water, creating a volume of 17.6 cubic centimeters,
 for it to enter in the negative electrode, the actual
volume of water is 17.3, so that there is a slight drying
out, so slight that we can't account fully for the decrease
in pressure as the state of charge was reached, but this
does show that there is a tendency in that direction.

So I am assuming that there is some other
mechanism that is going on inaddition to the opening of
the porosity of the negative electrode.

Now, this kind of explanation allows us to see
a compatibility with Von Doren's equation presented at the
Power Sources Conference in 1959, and with some earlier
kinetic measurements, indicating a pressure decay dependence
on the zero order on the state of charge of the negative
electrode.

With this as a background, we can go into
Turner's hysteresis. The purpose of the just previous
discussion was to set the stage for explaining the
hysteresis observed by Turner, which is shown in the next
figure.

May I have the next slide?

(Slide 18.)

Now the explanation that I had given earlier
about being able to change the state of charge of the
electrode by sintering out oxygen is shown in the upper
curve. This was two tenths of an ampere hour charge
ratio and up here, I believe it was 1.5. He took a ratio
of the state of charge of the negative to positive

CHEMICAL AND PHYSICAL EFFECTS

OF

INCREASING NEGATIVE ELECTRODE PRECHARGE

POS. $4OH^- \longrightarrow O_2 + 2H_2O + 4e^-$

NEG. $2Cd(OH)_2 + 4e^- \longrightarrow Cd + 4 OH^-$

NET $2Cd(OH)_2 \longrightarrow O_2 + 2H_2O + 2Cd$
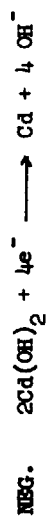
MOLAR VOLUME $Cd(OH)_2$	30.6 cm^3
MOLAR VOLUME Cd	13.0 cm^3
$\triangle$ VOLUME	17.6 cm^3

34% KOH	33% KOH	33% KOH
1333.1 g Soln	1322.4 g Soln	1373.3 g Soln
453.3 g KOH	436.4 g KOH	453.3 g KOH
879.8 g H2O	886.0 g H2O	920.0 g H2O
1000.0 cm3	1000.0 cm3	1038.7 cm3

	40.5 g Soln
	38.7 cm3

$\triangle$ M
$\triangle$ V

$\rho_{eff} \text{ H}_2O = 1.04 \text{ g/cm}^3$

$\triangle \bar{V} \text{ 18 g H}_2O = 17. \text{cm}^3$

FIGURE 17
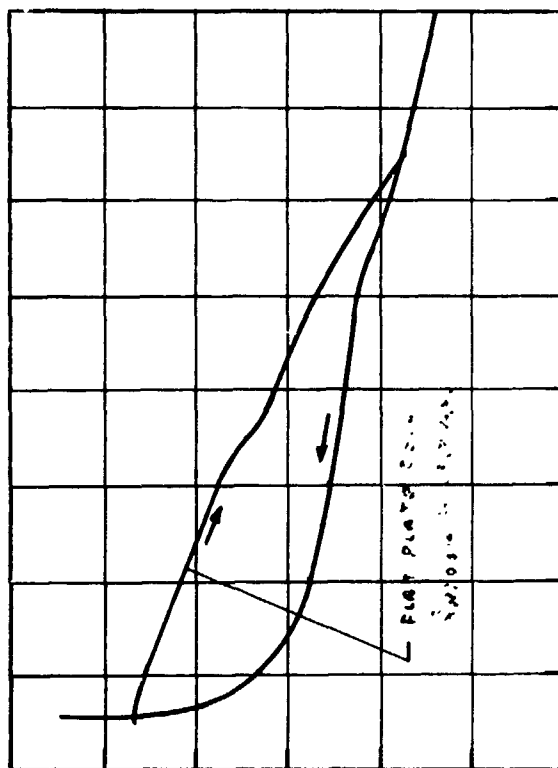
CHARGE RATIO Q_{Cd}/Q_{NiOOH}

Effect of state-of-charge of Cd electrode on
Steady-state oxygen pressure in Flat Ni-Cd sealed
cell on overcharge at 1.3 amp (~C/10).

FIGURE 18

capacity and expressed his data in terms of that charge
ratio, and the steady state pressures are on the ordinate
but if he vented out oxygen, which the sequential venting
out increased the state of charge of the negative
electrode, and then he backed up and as he observed the
hysteresis, they do not follow the same curve,that there
is a difference between them.

Well, the first plot, where I was dealing with
the effect, that small effect of having three tenths of
a cubic centimer residual void diminishing the effective
amount of electrolyte in the separator helps partly to
explain for the slope.

The other part would be that as this is going
on, as you are cycling it, there is an exchange of air
in the electrode, of the nitrogen in the electrode, into
the atmosphere of the cell, which he then vents off, and
with that, he essentially has less electrolyte in the
cell and he will follow the lower curve, so that the
amount of electrolyte between the two sets of electrodes
are different there, it is sequentially decreasing as it
is going timewise, down the scale, reversing and then coming
back.

And, again to take a quote from Turner, on
page 316 of the Power Sources Conference -- pardon me, of
the Journal of Electrochemical Technology, he notes, and
I quote:

"At times one finds that oxygen recombination
improves with time as some cells are continuously over-
charged after cycling."

So I guess we can summarize. Now, while there
are several mechanisms accounting for redistribution, one
is concerned with air entrapment at the time of filling of
the cells, and the evidence was presented for measurements
of 13 cubic centimeters of air that was entrapped in cells
that were filled and precharged in the usual manner as
compared to flooded cells precharged in an unusual manner.

Now by assuming such a mechanism, several questions
that have been answered less than satisfactorily were now
explained again, in part or fully, with this air entrapment
mechanism.

Now nitrogen is expected to be found in cells
if there is, indeed, air entrapment, and NAD Crane analysts
find more nitrogen in the cell than could be reasonably

explained by errors in sampling.

The electrolyte redistribution appears to account for the unexpected explosion that occurred in the cell at Crane, with the scavenger electrode, as well as for a loss of sensitivity of the oxygen sensing electrodes.

The electrolyte redistribution, in part, can account for the hysteresis effect discovered by Turner.

Now, by presenting an air entrapment or preventing an air entrapment on filling, not only may the problems that are a consequence of the electrolyte migration be avoided, but a natural transition could be made to polypropylene separators.

Thank you.

(Applause.)

HENNIGAN: Now, do we have any questions for Harvey Seiger.

Question right there.

QUESTION: You speak of air entrapment, is that at the vacuum filling?

SEIGER: Yes.

HENNIGAN: Any further questions? There is one right here.

PATIL: Arvind Patil, from W. R. Grace.

If the air entrapment mechanism is right, then shouldn't we expect similar kind of drawing in nylon separators?

SEIGER: But you have it. Tom Hennigan's second slide showed that the mass of material in the separator doesn't decrease with cycling, and I think it was Jerry Halpert that first found the electrolyte redistribution and those were in cells with nylon.

PATIL: No, but the intensity of drying in nylon is much less compared to that of the polypropylene. How would you account for that?

SEIGER: One of the reasons for that could be that the nylons are usually thicker, absorb more electrolyte, and you start with more.

HENNIGAN: We have another question in the back of the room.

HAAS: Hass, Philco Ford.

I have noted on a vacuum gauge for cells with a gauge assembly, let's say after six months of operation, we note that we still have a good vacuum in the cell and that we haven't noticed a change in the pressure.

What would be the reason for this?

SEIGER: Possibly -- it might possibly be that the rate at which this transfer occurs depends upon the use of the cell. I believe that cells in synchronous orbit do not show the same extent as cells that are in earth orbit, and when one compares, say, one year of cycling data, we are pulling out -- oh, I did a calculation at an average 40 percent depth of discharge -- we are pulling out something close to 40,000 ampere hours from 20 ampere hour cells that are cycled with low earth at 40 percent depth of discharge, we will have something in the order of 1200 ampere hours on a synchronous averaging 40 percent depth during the synchronous periods.

HENNIGAN: Bob Steinhauer.

STEINHAUER: Yes. Harvey, two things.

One, you discounted the corrosion of the positive plate very lightly, and do you have reason to do so.

And, second, do you have reason to believe this air is entrapped in a particular location in the cell?

SEIGER: Let me answer the second question first.

I believe that it is entrapped in the negative electrode. I have some preliminary data. The reason I didn't present these data was because of the way that they were taken. It is only individual electrodes, and with this type of experimental material, we should have a signif- icant number, say 10 or 20 electrodes, and then do a comparison and actually treat such data statistically.

It is a little difficult to see, but I have the pickup of 30 percent KOH, in grams of 30 percent KOH per gram of electrode, and if one merely immerses the positive and the negative electrode in electrolyte, they both pick up --

Could you clarify that a little? Okay.

We find that the positive electrodes on simple emersion will pick up .127 grams of KOH per gram of electrode.

If we then pull a vacuum on it, and this happens to be the same electrode, we get .15 grams.

Now, if we take another electrode and pull a vacuum first, and then introduce the electrolyte while it is in vacuum, you notice that we have .143, which is pretty good in doing that, and that is why we need more data to show whether there are differences and where they occur.

On the negatives, however, we start with .086, then we introduce it into vacuum, and there is an increase.

Now I actually used more vaccum to get this number than would be used in the cell.

And then we took another negative electrode, evacuated it first, and we find that we strike up much more electrolyte.

Well, I took an average between these numbers and compared it to that and did a calculation, and I come up with 10.5 CCs, due to the way it was impregnated with electrolyte, and then I wondered, gee, where are the other two and a half CCs, and I remembered I precharged these cells about 6 ampere hours.

So with the 6 ampere hour precharge, if you remember some earlier numbers that we had up there, the electrolyte volume or void space would be increased another 2 milliliters by the 6 ampere hours of precharge.

So, even moving this way, with such preliminary data, it kind of confirms that now there are three ways in which we are coming to the same number, about 13 milliliters of air entrapped.

What was the other question, Bob?

STEINHAUER: Corrosion mechanism.

SEIGER: The corrosion mechanism was the part that I had left out of this presentation to keep it down to a half hour, and I happen to have three slides and I think I would need about another 10 or 15 minutes.

HENNIGAN: Okay, do you want to make it 10.

SEIGER: I have three slides, three more viewgraphs. Let me get them.

First, we know that there has to be some kind of corrosion that occurs in the cell, because we see it becoming black.

Now, let's explain the corrosion. So we are really working here with what is known in logic as a method of reductio ad absurdum, in which we are going to assume there there is corrosion going on, and let's substantiate it.

Okay. We take nickel, and this is a very unlikely mechanism for it to occur, in replacing hydrogen, we do not get such a displacement reaction. Thermodynamics says it doesn't, but we will continue anyway, because after we get this nickelous hydroxide, we charge it up and we find that we need cadmium to charge it, and we wind up with hydrogen form, with, let's assume, one ampere hour of nickel hydroxide, that we can now measure, which would be an increase of capacity.

And we wind up with more -- with four ampere hours of cadmium and our comment is that this mechanism requires one ampere hour negative charge for one ampere hour increase to the corrosion, and, this hydrogen.

Okay, now so we have a set task. What do we do with the hydrogen, if such a thing comes on?

So we assume again 82 milliliters of gas void volume, that is 150 psi, we would know that. Gas leak rate, I can't think of any particular mechanism for it to come out. I would have to relate it to the helium leak rate, and it would be 1.4 times the helium leak rate, which is negligible, and therefore, the hydrogen is still negligible.

Okay. How else can we get rid of hydrogen in the cell? Let it reduce to cadmium. But if we reduce cadmium and then add this reaction to that one, we come

up with an overall that says 3 ampere hour increase in the negative state of charge for each ampere hour increase in the positive.

Now, if we do the same with the nickel oxide reduction, we wind up with again, with this, which may be occurring at a slow rate, _____ reported something on this nickel hydrogen that indicated that this reaction is probably going on, that there is a self-discharge in the system, and if this is going on, then we can consume hydrogen, and here is our overall reaction.

(Slide 19.)

And again we note that there is a 3 ampere hour increase in the negative state of charge for each ampere hour increase in the positive capacity.

Let's remember that and go on to our next mechanism for corrosion.

(Slide 20.)

And this is the one that I prefer. I think this is the one that is responsible for the blackening of the tabs, in which you are electrolytically oxidizing nickel di   ly up to the nickel hydroxide free electron change, and the cadmium has to go along. That is the source of the electron for it to go on, and we wind up again with the net reaction that says that there is a 3 ampere hour increase in the negative state of charge for each ampere hour increase in the positive capacity, so now we have a beautiful test for corrosion.

Either we are going to have hydrogen in the cell, and we know that we don't, so we can rule that out, or we are going to have, to find that the precharge in the negative has increased 3 ampere hours for each ampere hour increase in the positive electrode, and with that kind of information, we can go into the literature again and see what kind of data have been reported, and I go to a report with TRW back in 1969, in which, during an experiment, 6 cells were destroyed before and after a cycling regime, and it was during the cycling regime that the capacity of the cells increased.

May I have the last slide, please?

(Slide   21.)

CORROSION CALCULATIONS

TYPE II (OXIDATIVE CORROSION)

$$Ni + 3 \ OH^- \xrightarrow{3e} Ni \ OOH + H_2O + 3e^-$$

$$\tfrac{3}{2} Ca(OH)_2 + 3e^- \xrightarrow{3e} \tfrac{3}{2} Ca + 3 \ OH^-$$

$$Ni + \tfrac{3}{2} Ca(OH)_2 \longrightarrow Ni \ OOH + \tfrac{3}{2} Ca + H_2O$$

COMMENT: 3Ah increase in negative state of charge for each Ah increase in positive capacity. Water produced.

FIGURE 20

FIGURE 21

FIGURE 19

41A

In the upper part of the slide, we show the capacity of the positive by the bar graph, and the hatch means it is charged.

The capacity of the negative is shown by the adjacent bar graph. The state of charge of the negative electrode is indicated by the cross-hatching, and these are the results for 6 cells, each one destroyed.

It shows the uniform capacity on the positive. It shows the kind of precharge on each of the negatives, and then the cells were cycled through 72 cycles, I believe, they were that type of cycling, and afterwards, another cell from each of those six groups was destroyed, and the same kind of data obtained, in which we now show the capacity of the positives the same way, but you can see that there is a definite increase of capacity in the positive electrodes.

And the precharge, if you look, remains pretty much the same. A more quantitative look at such data shows that there is, indeed, a one to one relationship, that when the positive electrodes increased in this experiment by one ampere hour, the negative state of charge increased one ampere hour, which is not consistent with the corrosion mechanism.

So I reject the corrosion mechanism based on this evidence.

HENNIGAN: Do we have any more further questions of Harvey. Maybe towards the end of the session this morning we can have any other questions you come up; we will save a little time for questions then, that you could ask any of the speakers.

We have one here. Aaron Fisher.

FISHER: Fisher, Goddard.

I noticed before you answered a question that you have entrapment even after vaccum fill, so what is the preferred method now to avoid entrapment?

SEIGER: That is like asking me how I do it.

(Laughter.)

There is a way of getting it out.

FISHER: Okay.

VOICE: Tom, I think since the coffee has been here for a while, we should go ahead and take a break.

HENNIGAN: Yes, okay. I was just going to mention,too, that we are going to eat lunch late today, 1:00 o'clock, because of the several other meetings that are going on here.

(Recess.)

HALPERT: Gentlemen, could we please take our seats.

If you are planning to speak, either this afternoon or tomorrow morning in Floyd's session, this afternoon in my session or tomorrow in Floyd's, would you please make sure that you chat with us sometime during the day, and we have some three by five cards we would like you to fill out with your name and title, so we make sure we include you. So, please, sometime during the day, see either one of us and tell us about your slide requirements, if there are any.

At this time, before we continue with the separator section, Floyd Ford of Goddard has made up a survey, which discusses both the battery spec, one survey for the battery spec and one for storage, and he is going to briefly describe them, they are being handed out at this time, and we would like to have them filled out sometime today and returned, so that we can tabulate them and present them for your own interest tomorrow morning.

At this point I will turn it over to Floyd Ford, who will describe the two surveys.

FORD: Well, this year we decided we would try something a little bit different. It is always nice to have a little variety in any meeting, and we are trying to feel out you, as the manufacturers, you, as the user, what you think about some of the problems that we are now involved with.

There are two areas that we are distributing the survey, one is on storage, and we are trying to determine experience, the various experiences in the industry, with the storage of cells.

Now I realize that there are many, many questions that we all have, but we couldn't possibly put these down on a single survey.

There are those that may feel like they don't have the experience to fill this out or would not care to fill it out, then feel free not to do so.

I will point out we have not asked for names, of individuals or the company that you work for, because we really don't feel like that is important in the information we are looking for. However, if you care to put your name on it, or your company, that is your choice, and we would appreciate it if you do, but there is no obligation to do so.

Particularly in the area of specifications, we are currently revising the Goddard version of the interim model spec that came out a few years ago, that actually evolved form this type of meeting.

I would like serious critiques, serious comments, and good suggestions from you, because I can assure you that the inputs we get on this document, pro or con, will be given every consideration in the final revision of this specification.

So I will state particularly to t e manufactuers, here is a chance to get back at us, so let us have it.

Thank you.

HALPERT: Okay. Thank you, Floyd, and we will turn the meeting now back to Tom.

One suggestion please, for the speakers, wear this microphone around your neck and try and speak into it rather than away from it. We have had some problems with the amplification system, and I think it has been adjusted properly now.

HENNIGAN: Our next two speakers this morning will be from battery companies, Eagle-Picher and General Electric, who would like to go over some of their data on separators and what types of separators they are looking at.

Our first speak is Earl Carr, of Eagle-Picher.

Is Earl here?

CARR: Tom asked me to say in five minutes about the types of cells that we are building, with different separators, so I just want to give a brief history of, let's say, nylon versus polypropylene.

We started out with looking at cells with non-woven polypropylene approximately ten years ago, and a few years before that we started working with the nonwoven nylon separators.

The first cells that we built with polypropylene were for a designed experiment and an 8 ampere hour sealed cell.

In general, the conclusions of this designed experiment were that we had more recombination capability with the polypropylene, slightly lower capacity, but improved charge retention.

A couple of years following that, we designed a line of six different sealed cells from three and a half to 36 ampere hours, in which we used a two-layer separator design.

This is somewhat unique, I think, and what the thinking was at the time was that we would use the poly-propylene for its particular characteristics, in other words, oxidation resistance and its long-life type characteristics, and we would use the nylon because of its absorption.

We built these cells and we put them through an extensive series of electrical and environmental tests and also we did over 1000 cycles at 60 percent depth of discharge.

The data,in summary,was that after 1000 cycles, we measured full capacity on the cell, and we had over 90 percent of its initial capacity to one volt.

Now, then, the rest of the capacity was probably there, but it was below one volt.

More recently, we provided cells for the work that Tom Hennigan has reported on this morning, and I would like to show Table 1.

(Slide 22.)

You have seen this once before, so I won't really

elaborate on it, but this lists the different separators that were used in the 6 ampere hour cells and other treatments that they were given.

These are the cells that were cycled for 6000 cycles and subjected to the post morten analyses as reported by Tom Hennigan and Dr. Fisher.

Now we are also under contract through NASA-Goddard to supply a second series of 6 ampere hour separator test cells. And the separators that have been tentatively selected for these cells are shown in the next slide.

(Slide 23.)

I will spend a little bit more time here because the selection of these separators is based, in part, on the results of the first program.

The 2505 pelon has been included, necessarily, as a control. We felt also that another nylon would be advantageous to the program, so we have a W. R. Grace material, 2 ounce per square yard material.

In the nonwoven polypropylenes, there is a --

Why don't you slide that all the way up, Tom.

Okay. We have for the Hercules, we have two different weights. We have a 2 ounce per square yard, -- and let's see, I think I missed one there -- also the one and a half ounce per square yard is also to be included in the project.

I am sorry, there is a mistake on the slide, and that number should be 56, I believe.

Okay.

The two materials to be tested on the. Hercules are the 2711-55 and 56, with no treatment, and with a radiated   treatment per RAI, to improve the wettability.

On Kendall, we tentatively included XM-1249. On

W. R. Grace, there are three varieities. This is the one and a half ounce per square yard, and the one ounce per square yard of material. One radiated -- or, each of those radiated and the heavier material, with a wetting agent added to the material, or to the cell, actually.

Then we include the GAF material, using Hercules 90 as a wetting agent, and then the material designated P4212-S, which is a radiated WEX 1242.

Now, in summary, the reason for the selection of these materials is because it appears beneficial to have a permanent wetting capability for the separators. It has been somewhat concluded that it is advantageous for long life and for minimum cadmium penetration through separators to have a separator with a high wetting capability.

That is all for that, Tom.

In addition to the 6 ampere hour programs,we are conducting other programs and I want to specifically mention the large cell work that we are doing.

We are conducting separator evaluation testing on 50 ampere hour nickel cadmium cells. These cells are very similar to those used in Air Force classified satellites which are currently in orbit.

Mr. Marty Gandell of Lockheed presented a talk last year at this workshop, in which he summarized the results to date of an accelerated test program using four different separators on 50 ampere hour cells.

Briefly, these cells, there were four types, there were two nylons, and there were two polypropylenes, included. The two nylons were 2505 and 2506. Both used to be designated ML.

And we also have the two polypropylenes, which are WEX 1242 and FT 2140.

The cell thinckness was varied to obtain the same electrode spacing. It turns out that the 2506 thickness and the FT-2140 thickness are essentially the same, but they are different from 2505 and from WEX 1242, which are thicker materials. These last two are about the e thickness.

So the cells then are essentially two sizes, the only difference being the thickness of the cell, and these have been subjected to many cycles in an orbit simulation accelerated test.

The test was accelerated by performing a 45-minute orbit instead of a 90-minute orbit, and thus doubling the rates of charge and discharge in order to obtain more cycles in a shorter period of time.

The test is being conducted at 40 to 50 degrees F., and at this time we have completed 13,000 cycles on these cells, at an 11 percent depth of discharge, and the tests are continuing.

(Slide 24.)

The next slide shows a second generation of cells of this type.

These cells -- these separators are being evaluated in 50 ampere hour cells and some of them are also being evaluated in 110 ampere hour cells.

Briefly, I think most of you are familiar with the different separators. I don't really have any special words regarding these. The tests are in process. Right now we are in the early stages. They have not been placed on cycle yet. Certain of these will be placed on cycle to obtain further data.

I would just like to say in closing that it is very difficult to select a separator for cells. The first thing is that you can determine that it will work in the cell rather early, and that, in fact, the resistance of the cell is a pretty good measurement on a new cell, whether or not it is going to work new.

Dr. Fisher pointed out that there was a change of internal resistance of the cells. I seem to remember numbers like from three to ten milliohms, something like that, during 6000 cycles that he presented earlier.

The resistance does appear to be significant measure of whether or not it is a workable system and then once you have that, then, of course, the next thing to do is to cycle test them.

We have not come up with a better means as of this

FIGURE 22

FY71
SEPARATOR TEST CELLS
RSN - 6 TYPE

MATERIAL	MANUFACTURER	OTHER TREATMENTS	DESIGNATION
Non-woven Nylon	Pellon	None	2505
Non-woven Nylon	Pellon	None	2505KA
Non-woven Nylon	Pellon	Washed in 0.75 HCl/H2O	2505KAW
Non-woven Polypropylene	Pellon	None	FT-2140
Non-woven Polypropylene	Hercules	None	RT-97-2665-15
Non-woven Polypropylene	GAF	None	WEX-1242
Non-woven Polypropylene	GAF	Washed in Methanol	WEX-1242TW
Non-woven Polypropylene	Kendall	None	E-1451
Non-woven Polypropylene	Kendall	Washed in Methanol	E-1451W
Non-woven Polypropylene	Kendall	Washed in Methanol and treated in conc. H2SO4 & DI H2O Rinse	E-1451T

FIGURE 23

FY73
SEPARATOR TEST CELLS
RSN-6 TYPE
NAS 5-17806

MATERIAL	MANUFACTURER	OTHER TREATMENTS	DESIGNATION
Non-woven Nylon	Pellon	None	2505
"	W. R. Grace	None	3073-38(2oz/yd.²)
"	Hercules	None	2711-55 (I 5oz/yd²)
Non-woven Polypropylene	Hercules	None	2711-56(2oz/yd²) 2711-56(2.5oz/yd²)
"	Hercules	Radiated	2711-56X
"	Hercules	Radiated	2711-55X
"	Kendall	None	XM-1249
"	W. R. Grace	Radiated	3073-23X (1.5oz/yd²)
"	W. R. Grace	Add Wetting Agent	3073-23WA or 3073-32
"	W. R. Grace	Radiated	3073-23X (1oz/yd²)
"	GAF	w/Hercules 90	WEX1242 ISIS
"	RAI/GAF	WEX1242 Radiated	P4212-S

FIGURE 24

SEPARATOR TEST CELL
50-110 AH TYPES

MATERIAL	MANUFACTURER	OTHER TREATMENTS	DESIGNATION
Non-woven Nylon	Pellon	None	2505
"	Pellon	None	2506
Non-Woven Polypropylene	Pellon	Methanol Washed	T-21047W
"	Pellon	Methanol Washed	T-21092W
"	GAF	Methanol Washed	WEX-1242 W
"	RAI/GAF	WEX-1242 Radiated	P4212-S
"	W. R. Grace	None	3073-22
"	Kendall	None	XM-1249
50% PP 50% Nylon	Kendall	Methanol Washed	EM-490W

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date to say that it is going to work for three or five years, than to test it for three to five years.

We have not yet accomplished the accelerated test that was requested this morning in our introductory remarks.

HENNIGAN: Are there any questions for Earl Carr?

Will Scott.

SCOTT: Scott, from TRW.

Could you tell us how much electrolyte, based on cell capacity, was in these different 50 ampere hour cells, the four, especially the four types that you gave us the data on a little earlier?

CARR: Yes.

I don't remember exactly the number. It is in the neighborhood of three and a half ampere hours -- 3.5 CCs per ampere hour. It is not any more than 3.5 CCs per ampere hour.

SCOTT: Are you saying then that you use the same ratio in the polypropylene cells as you did in the nylon cells?

CARR: I don't know. I don't remember.

HENNIGAN: Are there any more questions for Earl Carr?

(Discussion off the record.)

HENNIGAN: Thank you very much, Earl.

Then our next speaker will be Guy Rampell, from General Electric, on some of the separators that they are evaluating.

RAMPELL: We have started an evaluation of some polypropylene separators.

(Slide 25.)

As shown on the first slide, we are looking at

two Hercules separators of different weights, primarily, and two Grace materials.

I want to point out, though, that the Grace materials were made at Esso and those samples are limited. They do not represent production available material.

The materials for the KOH absorption column were done by vacuum impregnation, irrespective of whether or not the material had wetting properties.

In the case of polypropylenes, we used vacuum impregnation. We feel that this gives us a more accurate percentage of absorption.

The technique beyond that is to rub off the last remaining drops onto a plastic plate and the results seem pretty reproducible for like samples, by the technique, providing, I guess, if you use vacuum. The weight is done by actual measurement and has no bearing on the claim weight, except, I will say one thing, perhaps the figures might be closer to what is represented by the manufacturer, if you condition the fiber first by drying out for 24 hours or something of that sort. We didn't do that.

The thickness is given and is slightly under a little bit more compression than you can get on a caddy gauge.

I would like to point out that the KOH absorption is influenced by type of wetting agents, by fiber diameter, by fiber density, and so it is pretty relative to those conditions, and has to be taken into account when you evaluate separators, just exactly what are the additives in or on the fibers, and the percentage of additives and contaminants.

Aside from the electrolyte distribution mechanism that we heard about this morning, I would like to point out another phenomena that is a well-known phenomena, but I would like to bring it to our attention, and that is that there is electrolyte movement with every cycle.

At the end of every charge, for example, the electrolyte moves into the separator system in greater quantities than at other times during the cycle, and depending upon the interelectrode distances, the

compression on the separator, and the KOH absorption of the separator at this particular time, say cycle 0 to 50, the separator may or may not hold all of the electrolyte that comes out of the electrodes at the end of charge. If it does not hold it, it will go into the free volume spaces in the cell, and this can be a problem with some of the lower absorption separators.

And, also, the KOH absorption units given there can change as life progresses. The additives may or may not be subject to movement, the solubility in the KOH may change, they may be oxidized to some extent by the positive plate in the oxygen atmosphere, so those things have to be taken into account, particularly electrolyte movement and supersaturation.

The fiber diameter and the density and the electrolyte movement all have some effect on just where the cadmium migration is going to stay. You are going to get cadmium migration but we are trying to restrict it to the cadmium side of the electrode.

In general, the microdiameter fibers seem to be a better filter in that regard.

I think we can go to the next slide, now.

(Slide 26.)

This is cycling of those four separators in an 8-hour orbit. We call it an accelerated bype of cycling from the standpoint of the case temperature that we are running it at. We are running it at 30 degrees centigrade and 70 percent depth of discharge, a six-hour charge, two-hour discharge.

The end of discharge voltage is given on the vertical axis, and if you raise it just a little bit, Tom, we have the number of cycles to date.

There aren't very many cycles. The test has really just commenced in the last two or three months, and, we are not drawing any conclusions from the test at this particular time, because, for one thing, there may be crossovers on the various separators later on, and we certainly expect some plateauing, also, and then we will look at the various parameters and failure mechanisms and degree of cadmium migration by analyzing the separator, the amount of KOH retention.
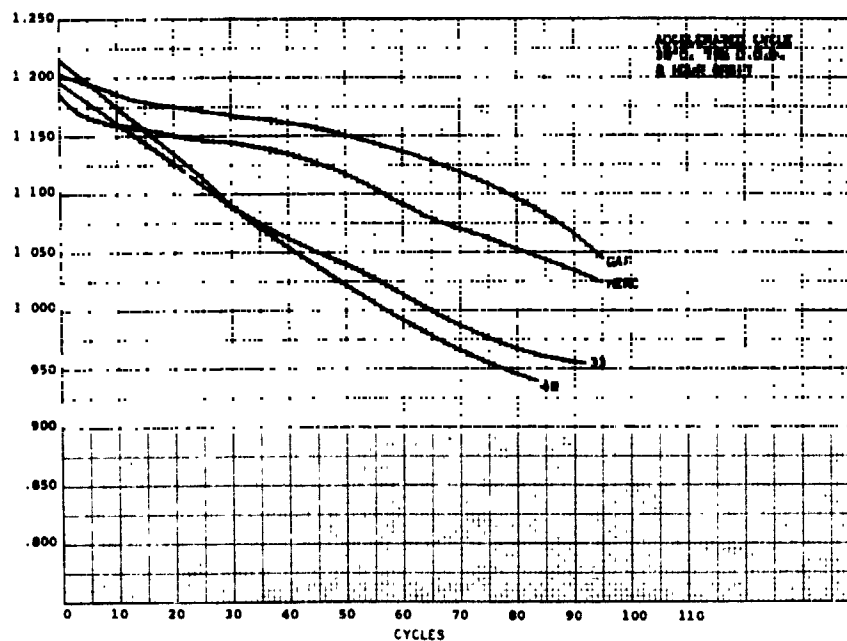
FIGURE 25

SEPARATOR TYPE	AIR PERMEABILITY CFM/FT^2/0.5"H$_2$O	KOH ABSORPTION	WEIGHT OZ/ YD^2	THICKNESS(MILS)
GAF	115.4	243%	1.97	9.1
HERCULES 1.5 OZ	48.0	840%	1.74	10.9
HERCULES 2.0 OZ	-	915%	2.12	12.5
W.R. GRACE #33	30.9	833%	1.91	10.8
W.R. GRACE #48	171.7	543%	2.45	15.1

FIGURE 26

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Right at the moment, GAF seems to be producing a slightly higher voltage with the Hercules separator, right close to it, the Grace materials are somewhat down at the moment.

The cells are 6 amp hour cells, and, as I say, we are really trying to accelerate what we know about cadmium migration, and that is to run it a high temperature, with high DODs.

500 of these kind of cycles would be equivalent to, I would say, three to four thousand cycles at 25 percent DOD in a 90-minute orbit, in our opinion.

I think that is about it, Tom.

HENNIGAN: Thank you, Guy.

Any questions for Guy Rampei ?

Question back there.

Steve Gaston, did you haveone? Okay.

GASTON: Guy, did you have any wetting agents in thos polypropylenes? If so, what types were they or did you make an attempt to wash them out? It wasn't too clear to me.

RAMPEL': Steve, those fibers were as received and so that in the case of GAF, we are told with Hercules 90, some other people have told us they have analyzed it and found it to be some Triton 100, so I really don't know what is on the GAF fiber.

I guess I want to say that in the case of Hercules, there is a wetting agent on that fiber also, and the Grace 3, I have been told has a wetting agent incorporated in the resin at the time it is blown.

The 48, I believe has no wetting agent.

HENNIGAN: Bob Steinhauer.

STEINHAUER: Are you running -- I recognize this is a high temperature test, but are you running nylon controls along with this to show where that data would fall?

RAMPELL: No, I don't have any control, Bob, of nylon. I was running GAF as a control.

STEINHAUER: The reason I bring that up is that we collectively think we know the properties of nylon, but when it comes to justifying flight use of polypropylene, it is very valuable to have a point of nylon, even though it is degrading, to show it and run it as a control. It helps on these justifications.

RAMPEL : I think your point is well taken. I just didn't want to run the risk in this series connection, I am running these cells as a battery and I didn't expect the nylon to last very long.

HENNIGAN: Joe ?

LACKNER: Lackner, Canadian Defense Research.

There seems to be some mention by previous speakers of a correlation between cadmium migration and the separator. Have you found any correlation between the drawing out for the cadmium migration as a function of the separator, or is it a function of the plate, and how the plate was made, and is there any way of retarding the cadmium migration?

RAMPEL : Yes, I would respond to your latter request for retarding cadmium migration. Last year, NASA-Goddard had a paper showing that teflonated negatives would retard cadmium migration to very, very significant extents, but I guess that your real question here today is the influence of the separator on cadmium migration or possibly the makeup of the plate.

I think that cadmium migration can be influenced by the separator to the extent to which this flow of electrolyte you get between the end of charge and discharge, the temperature that you are using promotes migration. The depth of discharge promotes migration and the amount of electrolyte itself, that the cadimium can dissolve into, and the degree of movement inside or outside the separator, all has an effect on the cadmium migration.

HENNIGAN: Vince.
(Inaudible.)
D'AGOSTINO: The reason I bring this up is we have looked at a number of polypropylenes and we found that they had the same absorption when they were prewashed or when they were not. However, any separator that you wash with methylene choloride, would have essentially zero wicking characteristics. I odn't know the effect of that on batteries.

RAMPEL : We did not do any wicking experiments, primarily because in aerospace cells, we rely on vacuum impregnation to wet the separator, and we really don't care if it takes all day for the separator to wet or not, so long as we can wet it immediately with vacuum impregnation.

VOICE: The only point I am trying to make is that if you see a transport of electrolyte in your cell, and that is essentially washing out some of your wetting agent, it could, on a long term, make rewetting of the separator itself rather difficult.

RAMPEL : Right.

HENNIGAN: Joel Bacher.

BACHER: Bacher, RCA.

Do you have any specific effects to which you attribute the difference in voltage levels to the different separators?

RAMPELL: I didn't take the resistance of the separators, Joel, and I think the other reason though is that with these different separators, we try to, there may not be enough electrolyte in some of the cells. That's a possibility, to begin with.

HENNIGAN: That is all the questions, okay, thank you, Guy.

Joel, I would like to answer your question there, on the tests that we ran. All those cells decay in voltage, I don't care whether you are using nylon or polypropylene. It is the usual thing, when we make capacity checks about every three months, we bring them back up again, and so no matter what material we have in there, or how much electrolyte, they all did the same thing in that respect, at least for the first 4500 cycles, then we had troubles with some of the cells.

They were all about the same magnitude, too, that was kind of strange.

I showed some of that data last year, and I didn't have the time this year to go over it again.

Let's see, our next speaker is from TRW, Dr.

Willard Scott, who has a few words on separators also.

SCOTT: Before talking about what I basically have to say, which is some of our recent experience with polypropylene separators, I would like to make a few comments on some of the discussions that have gone on previously. I have saved up a few here, to let you have it all at once, while I was up here now.

First of all, regarding the results that Tom presented, I believe I am correct when I am saying that in general, probably all the cells that were tested that had polypropylene separators in them, started out with a significantly lower volume of electrolyte in the cells than did the cells with nylon separators. I may be wrong, but I believe that is correct.

So, that if there is a redistribution problem, such as Harvey has proposed, it seems to me that the cells with -- such cells with polypropylene separators, start out with two strikes against them, as opposed to one or a half a strike with the nylon separator.

So I think that factor has to be considered in evaluating the results that Tom presented to you.

One other point, regarding those results, also, as Bob Steinhauer pointed out, one has to look at the results a little bit critically, as they may or may not apply to applications in synchronous equatorial orbit.

I believe it is true that if you look at the trends of the data, say, within the first one or two thousand cycles, rather than just focusing on 6000 cycles, you see relatively little change in the characteristics of the cells since they were new, and this may suggest that the problems that you may encounter, if you try to use polypropylene separators, in a synchronous equatorial orbit, with much fewer cycles to contend with, may be much less than might be suggested by the data for 6000 cycles, as applicable to the lower earth orbit.

It is true, of course, that normally one uses a much higher depth of discharge in a synchronous orbit application, because you can get away with the larger depth because of the fewer number of cycles, and it is probably true that the problems of electrolyte and of drying become more severe as you increase the depth of discharge.

So you can't just simply equate cycles for cycles for 25 percent depth versus 60 or more so percent depth.

I don't know what the equation is relating these two depths of discharge, as far as electrolyte problems are concerned, but I just wanted to point out that it is possible that the problem of applying polypropylene separators at the present state of the art to a synchronous orbit may be, where, say you have a, let's say, five to seven hundred cycle maximum requirement, maybe in order of magnitude simpler to solve than those for a five-year low earth orbit, where you may have twenty to twenty-five thousand cycles.

The comment on the piece of data that was shown for the wettability of polypropylenes after extraction, after cycling, where it indicated that they were extremely nonwettable, this is, of course, very interesting, and a little bit puzzling, because that characteristic, at least, those figures do not appear to correlate with the performance of the cells containing those separators.

I would not necessarily expect a direct relationship; however, if, indeed, the wettability as measured by that technique, if the cell responds in the same way at all to that kind of wettability number, you would expect the cells to have been out of commission long since.

So there is probably -- of course, many different factors are involved in an actual cell, not the least of which one would be the fact that you have, of course, the separators in intimate contact with the plates, which do retain the electrolyte and there is obviously an inter-change between the electrolyte and the pores of the plates and the contacting separator material, and you must -- obviously there must be a transfer of electrolyte into the separator, or an exchange there that is not reflected by the measurements that we have seen this morning.

Now, one more comment on Harvey Seiger's presentation: In my view, the potential, or the impact of the type of electrolyte redistribution that he has proposed, could be extremely large, as far as I am concerned.

One of the questions it raises in my mind is whether we are using the proper criteria for deciding how much electrolyte to put in the cell at all these days,

because if, indeed, there is a -- if redistribution begins, which it does, as soon as the cell begins to cycle, and one judges that he has the right amount of electrolyte by the performance of the cell at that point in time, it is obvious that that performance characteristic is going to change rapidly with cycling, and pretty soon you are not going to have the same performance, and so you are not going to have the same criteria that you can apply for whether you have enough or not enough electrolyte.

So that I submit that we should take a look at the whole procedure for deciding when you have enough or not enough electrolyte in a cell, and correlate this with trying to decide whether or not the electrolyte has reached some level of, well, let's say equilibrium, in terms of its redistribution into the plates.

I am particularly concerned that in connection again with polypropylene separators, that is where I guess the biggest rub now appears to be, that because of the particular characteristics of polypropylene, it is very -- it seems to be very easy right now to come up with a poor cell design based on the existing approach to setting the amount of electrolyte in a cell, which has been based primarily on the performance with nylon separators.

Now it is obvious that there a number of quantitative and qualitative differences in the interaction between the plates, separators and the electrolyte, whether or not you use nylon, and whether you use polypropylene.

And I think this situation needs to receive some careful attention.

Now, with that, then I just wanted to describe briefly what we have been doing with polypropylene, in approximately the past year.

It breaks down into two things. We have going at TRW a development program for the Air Force for developing and testing a long-life battery for synchronous equatorial orbit applications, and the intended target lifetime is seven years in orbit, which means something like at least a nine-year total useful cell life, including the usual amount of ground handling and testing that goes on, plus the fact that the Air Force would like to be able to store these batteries for 18 months after the battery is completed on the ground, prior to flight.

So, adding all this up, you can stretch this into a total of about a 10-year, actually, a 10-year, approximately, useful life, throughout -- well, from ground testing to the end of its orbital life.

We have selected a 50 ampere hour cell for the present development phase to manufacture a one kilowatt level battery for synchronous orbit applications.

At the present time, during this last year, we have received 36 50-ampere hour cells, and these are currently on tests.

The separator that we selected was the GAF/WEX 1242 for these cells.

The reasons for our selection are a little bit complicated. They are partially technical, and partially nontechnical, as often turns out.

The technical reasons involved some comparative tests between that separator and several others that were commercially available.

The point of commercial availability is that even though this is a development program, the intended use period is not too far away, and we were constrained to select separators that we felt reasonably confident could be produced reliably and uniformly, and in quantity, within the next few years.

Now that reduced the number of possibilities considerably.

So based on comparative tests that -- some of which were performed at General Electric, and others from other data, much of it you have seen today, and some of which you saw last year at this conference, mixed all up together, the answer came out GAF/WEX 1242.

We do not necessarily intend to build all the cells on this program with the same separator; however, we do intend to build enough cells to build three batteries, which will be put onto life test under this current program.

The additional cells then may be purchased with other separators for comparative testing.

For these 36 cells, we do not have a lot of life test data on to date. They were received in April of this year, and they are -- as weill be described in an interim annual report on this project, which is due out soon -- we have built one 24-cell battery and it is currently on a synchronous orbit real time life test.

We have completed a simulated -- one simulated eclipse season of 45 cycles of varying depth of discharge, upto a maximum discharge of 43 ampere hours in that cell.

We are purposely pushing the high end of the depth of discharge scale, and this is one of the more developmental aspects of our program.

All of the cells in the battery are performing uniformly at this time. The battery is currently on continuous trickle charge, where it will remain for another several months before we have some additional cycling, when the next simulated eclipse season comes around.

I will comment on the characteristics of the group. It was originally felt by the manufacturer that the use of -- first of all, let me say that we had purchased, approximately two eyars ago, about 20 50-ampere hour cells of a general physical design very close to the present design, but using pelon 2505 nylon separator material.

These cells have been around and been off and on tests most of that period of time, and it would be very -- it is very difficult   summarize that test history, but a summary of it will appear in the Interim Report, which I mentioned.

Generally speaking, we had 12 of these cells in a breadboard battery, that has experienced a total of approximately 330 cycles before we shut down that particular test. Most of the cycles nad been at a depth of discharge of between 40 and 45 ampere hours in this 50-ampere hour rated cell.

At the end of about 330 cycles, the capacity in the cells was -- the total capacity at 25 amperes to one volt of these cells was a little over 60 ampere hours.

The initial capacity of those cells two years

earlier was, averaged 62 ampere hours, under the same conditions.

So, that sort of gives you a bird's eye baseline as to how, at least the basic cell, with nylon, at least, can perform.

Now with the current lot of cells that I mentioned with polypropylene separators, they were built with -- as close to the same design of plate materials, same loading, and other factors, as we knew how to get, and it was originally felt by the manufacturer that because of the use of polypropylene, that the capacity of these cells would not be as great as the capacity of the cells with the nylon separator.

As a matter of fact, the average capacity, measured under the same conditions, of these more recent cells, was 65 ampere hours, and the voltage characteristics were not significantly different than the same cell with the nylon separator that we had been testing previously.

So I might say this is, as I say, this is at a 25 ampere hour, 25 ampere discharge rate. There is some evidence that at much higher discharge rates, you can see a significant difference in the voltage between nylon and polypropylene separators, but we did not see it significantly at 25 amperes in these cells.

The other thing I would like to say is that in addition to the 50 ampere hour cells, we have had a small number of 20 ampere hour cells that have accumulated a considerably greater cycle life.

We have six 20-ampere hour cells, which admittedly is not a big sample, but it is something. All have poly-propylene separators. Three have the older pelon FT-2140 separator material, and three have WEX-1242?

These cells have completed approximately 700 cycles on an 8-hour cycle basis, with a depth of discharge that has varied from time to time between 15 and 18 ampere hours in a 72-minute discharge period.

Five out of those cells, at this point in time, have end of discharge voltages above one volt. There is one cell that is slightly below one volt, at the end of discharge, at this time.

Interestingly enough, all three cells with FT-2140 are above 1.1 volts at this point in time, end of discharge voltage. The one cell that is below one volt has the WEX-1242 and so whether or not this is a significant difference, I don't really know yet. I suspect that from the appearnce of the voltage characteristic that we could be -- we could have an electrolyte problem here, because there is a varying quantity of electrolyte in these cells.

I want to say one -- I want to mention final aspect, and that is -- well, two things, if you will permit me.

One is that bared on the performance -- all of our 50-ampere hour cells have oxygen signal electrodes. Based on the performance of these electrodes in the cells with nylon separators, we started testing the new cells with polypropylene, using the same type of electrode and the same load resistor and, lo and behold, the signal levels were very much lower right off the bat, with a brand new cell than we saw -- ever saw in the nylon cells.

One correlating measurement, although I don't know what the exact relationship is yet, is that the impedance between the signal electrode and the negative electrode in these cells, measured at 60 cycles AC, was roughly 20 times that measured for nylon cell under a variety of conditions.

Also, by increasing the load resistor, from something like 50 to 100 ohms, on up toward 1000 ohms, we could generate a signal comparable to that that we were getting at 100 ohms out of a cell with nylon separators.

I don't understand exactly all that is happening here, but I believe that there is some significant differences in the behavior of an oxygen signal electrode, depending upon whether you put it into a cell with a nylon separator or into one with polypropylene.

Now, we may be in the same problem area again in terms of electrolyte distribution, as I have mentioned before. I am not sure yet.

However, I do believe that here, again, one must should be aware that the design of a cell with an oxygen sgnal electrode with polypropylene separators should be

done with a somewhat different approach and more information in mind than is available presently from experience with nylon separators.

One last, and possibly the most interesting coment, I would like to make, with regard to the use of polypropylene, under certain aspects and during certain periods of charging of the cells with oxygen signal electrodes and polypropylene separators, we got some very strange oxygen signal output characteristics.

I couldn't begin to really summarize them in graphical form, so I chose - -- I am choosing to be qualitative at this point, until we have a chance to analyze the data further.

But, basically, during certain portions of the charging cycle, the singal would drop precipitously, and in some cases, it was essentially zero for a certain period of time, and then near the end of charge, it would suddenly take off again, and assume a -- well,let's say a normal level, which, for that particular electrode, was still, of course, much lower than we had seen previously with nylon separators.

Eventually what happened was that we looked into what was really happening, and one of the devices that we used was a laboratory cell case that we had been using for other purposes at TRW, which -- in which we could put transparent plastic faces on the sides of the cell, so that we could look into the cell to see if we could see what was happening inside, if that would be of any benefit.

And the one viewgraph I have shows a photograph of the cell.

(Slide 27.)

I don't think we need to show the top there, Tom, the bottom half is what I wanted to show.

This is a take-apart cell case, cell design that we have been working with for a couple of years now, that consists of a polypropylene body, all around here, and there is just a series of holes around the outside through which screws may pass. This is an O ring all around here to make the seal, and of course, the various fittings on the top; a gland over here, which we can take out as many as four leads through a sealed compression teflcn

FIGURE 27

62A
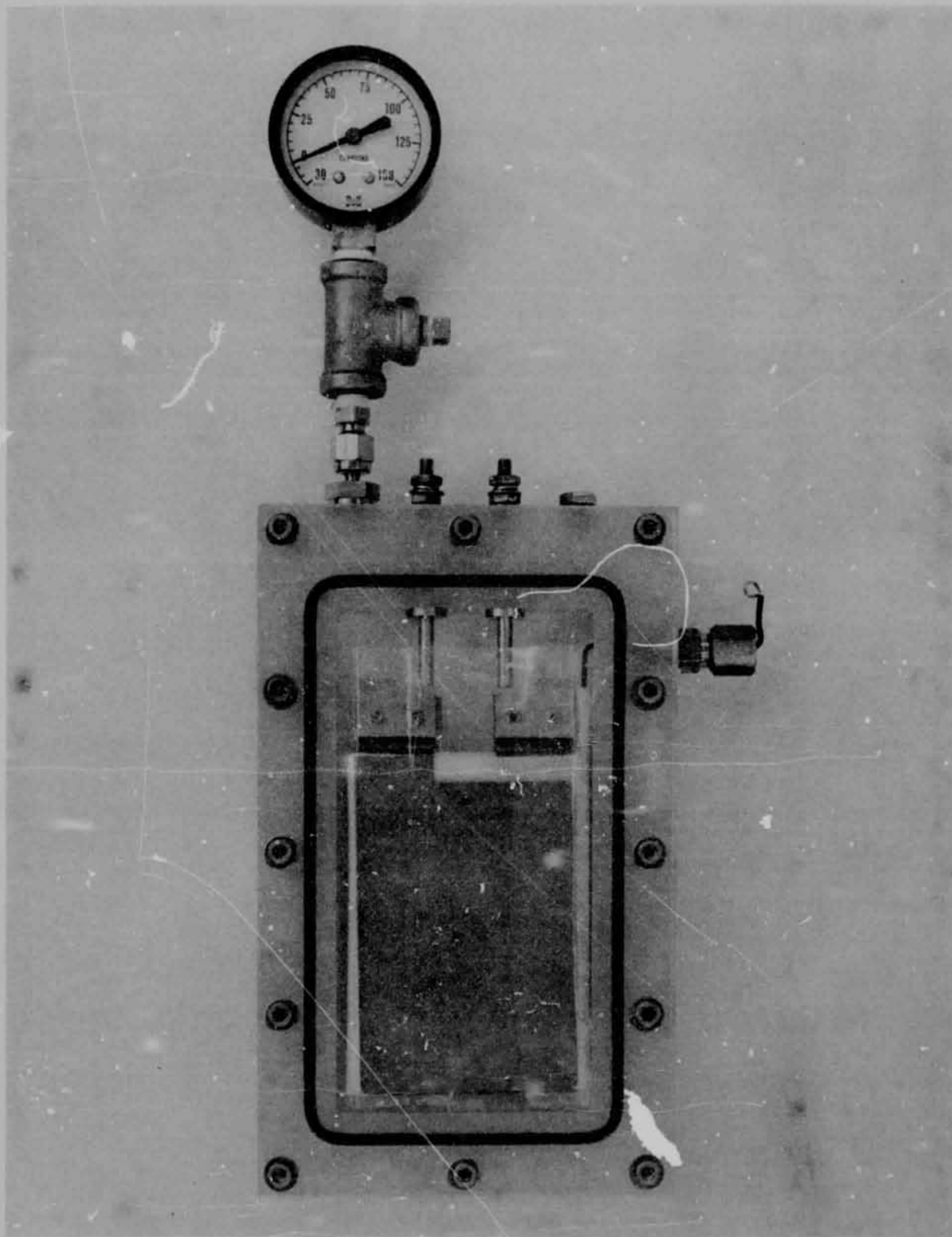
bushing.

And the photograph -- the particular photograph you see here is one in which we have put two quarter-inch lucite plates, one on each side, and clamped it down to form the cell.

We can put stainless steel plates, either one side or both sides, when we wish to keep the cell cool, we have to use a metal plate on at least one side or else the cell gets too warm because of the very low heat conductivity of the plastic.

So, well, you can see, these are the plates and the white material here is the separator, and this is just a polyethylene plastic bag that we use to wrap around the entire pack.

Well, using this type of cell, with the same separator system and the smae degree of interelectrode spacing and all of that that exists in the 50-ampere hour cell, we started charging this cell, watching what was going on, and, lo and behold, about halfway through charging, electrolyte comes pouring out of the pack and starts filling up the cell.

Now, one other factor that I guess I failed to mention, the location of the oxygen signal electrode in the 50-amp,36-50 ampere hour cells that I discussed, was over here along one of these edges, squeezed up against the pack, with appropriate shimming.

What we saw going on then was that a certain point in .charging, the electrolyte would come out of the pack, rise up here and complete submerge the electrode, and it was at that point where the oxygen signal decreased markedly and it was obvious that what was happening was we were flooding out the electrolyte and the oxygen was unable to diffuse rapidly through the liquid layer, and so that was what was happening.

Well, then we began asking ourselves which we would rather have, an unreliable oxygen signal, or that much electrolyte i. the cell, and it was apparent, our decision was that we did not want to further decrease the amount of electrolyte that was put into the cell, because we were already using considerably less in the cell than is normal for the same cell with nylon separators.

Also, we discovered that as you cycle the cell more and more, the amount of electrolyte that comes out becomes less and less, and this tends to, at least is consistent with the picture for electrolyte displacement of air or whatever in the pores that Harvey Seiger mentioned earlier.

At any rate, to make a long story short, what we have had to do and actually, we are still really looking at the problem, is to put the oxygen signal electrode back over here in the large space where it is under considerably different kind of restricted environment than it is over here on the edge, and this appears to be, at least, basically, an approach to a solution to our problem.

One thing we did observe, at least with polypropylene, is that the exact performance of the electode is extremely snesitive to the exact degree of compression ard the physical arrangement over here on the edge of the pack, whereas, it does not appear to be nearly as sensitive to those factors when you use nylon. The reason for that, I can only surmise right now, and I won't go into that.

I just want to mention that one has to be, as mentioned before, considerably more cautios or more aware of the factors which cause -- which relate to the performance of the oxygen signal electrode when polypropylene is used as the separator material.

That's it.

Thank you.

HENNIGAN: Are there any questions for Dr. Scott?

Steve Gaston?

GASTON: Gaston, Grumman.

I have two questions. One of them is what was the test temperature of the various test programs in which it was conducted and, the second question would be on the nylon-polypropylenes, were they as received or was the wetting agent removed?

SCOTT: Yes. All of the testing that I mentioned was done at an average cell temperature of I would say 40 degrees F. It is at that cool temperature range that we are doing almost all of our testing.

Second question, all of the materials that we have used for separators, as far as I am aware, are being used as, in the so-called "as received" condition.

HENNIGAN: Steinhauer?

STEINHAUER: Bill, you mentioned you tried to keep the plate design the same between these lots of two 50s and I don't know about the 20s, but are all of these three lots from the same cell manufacturer?

SCOTT: Yes, they are.

STEINHAUER: Second, just a comment.

On our near earth orbit program for the Air Force, we made a similar decision to favor the electrolyte level in the polypropylene cell at the expense of signal through the electrode.

HENNIGAN: Any other questions.

Joseph Lackner.

LACKNER: Lackner, DRB Canada.

On the tests you are running, how much of an overcharge were you putting into the cells and you said that with the cycling, the amount of electrolyte that ca: ɔ out decreased. Was there any way of getting that electrolyte to come back to the normal amount, or is this going to decrease the dryness?

SCOTT: For the testing on the 20 ampere hour cells, the overcharge-recharge ratio varies a little bit, depending upon variations in cell voltage and so forth, but I would say it is averaging 20 percent, maybe it might vary from 15 to 25 percent.

We are purposely testing under conditions where we do not want inadwquate charging to have anything to do with the results, if we can help it. In other words, we purposely probably are charging them maybe somewhat more than is absolutely necessary, because we wanted other factors to control the performance of the cell rather than incomplete charging.

LACKNER: Well, what would be the purpose of the oxygen electrode, if it is not a charge control?

SCOTT: No, I am sorry, there is a different objective in that 20 ampere hour test than in the battery test.

In the batteries, the battery design uses the third electrode signal as -- to switch the current down from a higher level to a lower level when adequate charge is received. This same charge method was not used with the 20 ampere hour cell test. That was just a time based test only.

LACKNER: On the second part of the question, about the drying out, is there any way of getting the electrolyte to come back to the normal, or is that just going to dry out, too?

SCOTT: Well, now, you say drying. No, I don't know whether it is dry or not. All I can say is that the amount of free electrolyte that can be seen outside of the pack decreases as cycles increase. And in some cases, tne decrease -- it disappeared completely. In others, it did not, so there appears to be a variable here in terms of the number of cycles that it takes in order to allow whatever redistribution or whatever is happening from cell to cell.

LACKNER: It never equilibrates or it --

SCOTT: Well, you --, now we have done something else, we have come in later on and put some more electrolyte into the cell, to see if it will take that up, and if you do this often enough, you do reach a point where no further -- no more electrolyte further is taken up, by the cell, and then it is just, the situation is stable. At that point, however, you have -- you do have. you know, essentially a flooded cell, and it isn't really suitable for use sealed any more, because you do generate pretty high pressures.

HENNIGAN: Ernst Cohn, do you have a question?

COHN: Yes, Cohn, NASA Headquarters.

To go right on with what you were just discussing now, it seems to me you have given us a method for eliminating the problem that Harvey Seiger talked about, namely, by cycling and by having this variable amount of air being displaced by electrolyte, and then adding as

much electrolyte as you may wish to, maybe not the full amount that you did, maybe something less, but in any case, it looks like you probably don't want to seal off these cells until you have replaced a certain amount of electrolyte, or added a certain amount of electrolyte, then seal them off, and then you won't have the problem of the oxygen electrode nor the problem with drying out.

Do you think this is a good method of getting more reliable, longer-lived cells?

SCOTT: Let me answer your question somewhat in reverse.

I believe it is absolutely essential to resolve this issue of where the electrolyte gets to and how fast in order to have uniform cells, in order to have -- generally, in order to increase the overall reliability of these cells.

Now, how you do it is a separate question, and a good one, of course.

I believe, it appears that cycling is probably too long and too variable a way of doing it. AS I mentioned, in some of these cells, it appeared that it may take several hundred cycles to cause an appreciable redistribution of electrolyte.

I would imagine that various vacuum filling techniques would probably, if done properly, would probably be much more quicker and maybe more practical.

FORD: Ford, NASA, Goddard.

In view of the discussion, I just wanted to make a comment. We have now, and I think if you view the proceeding of the last workshop and perhaps the one in 1970, you will see the word "burn in," or a reference to "burn in" period that we have discussed.

Now, this we have observed in electrical performance, and I don't think it is -- well, it appears to be quite obvious that you are seeing something that is probably correlatable to what we have seen in the electrical burn-in. The point being, this particular subject has been discussed in the past, and it is ironic that we are sitting here two years later, and I am sure it goes back two years,

and we are really talking about the same thing, because
I am convinced that every nickel cadmium cell that is ever
built exhibits a phenonenon that we have called "burn-in,"
particularly when subjected to cycling.

And it is an irreversible type operation, that
you never completely return to where you started on day
one.

SCOTT: But are you saying that all of the
aspects that you are talking about of burn-in might be
associated with the electrolyte and nothing else?

FORD: No, no. From our viewpoint that we
have been looking primarily at the chain in the
electrical characteristics. For instance today, to run a
set of parametric data on NICAD cells for low earth orbit
charge of design, the voltage limit involved, where you
are trying to come up with data to design a voltage
temperature control system, if you subject cells to
cycling, the first month of data is totally useless in
designing that voltage limit because you don't get the
same results after one month. I am talking about low
orbit cycling, 15, 25 percent depth. You don't see the
same results after one month that you saw in the first
couple of weeks. We see as much as 30 percent change in
the overcharge characteristics of cells which were subjected
to the same condition after 30 days.

HENNIGAN: Any more?

MAURER: I would like to comment on the problem
of gas redistribution that Harvey described.

If you put a porous body into a liquid and then
pull a vacuum on the surface of the liquid, gas pressure
deep within the pores of the body will equilibrate with the
capillary pressure of the liquid in the pores and therefore
you will not be able to get any more than a certain amount
out, depending on the pore size distribution of the
electrode, and, of course, if you put the electrolyte in
the cell and then pull the vacuum, you have the same
situation and as you cycle the cell eventually, it
redistributes as you have described, and the obvious way
around this is to pull a vacuum on the cell first, and then
add the electrolyte, then you won't have this problem.

There is another phenomenon that takes place
in the cell that was described in a paper by Fritz Will
a few years ago. concerned with the movement of cadmium

hydroxide and cadmium in and out of a pore or along the walls of a pore, due to the concentration cells that are set up.

On initial charge, especially fast charge, the cadmium electrode will be functioning mainly at the surface and so the change in porosity of the electrode will be limited to a surface layer, and I will not speculate on how deep that might be. It will depend on all the electrode parameters.

But, as the cell is cycled, discharged material will move in and you will -- the effective pore shape will change from a cone to a longer tube as material OO and the pore opens up deeper down and in the paper I presented last year on the oxygen pressure, the effect of negative structure on the oxygen pressure, I showed a curve of oxygen pressure versus negative loading.

As the loading goes up or the porosity comes down, then the pressure goes up by a drastic amount.

What really counts in the cell is not the total electrolyte volume but the ratio of the electrolyte quantity in the negative electrode to the porosity of the negative electrode, and if you change the state of charge on the heavily loaded negative, then the porosity will change by a large percentage, because the electrode 's not very porous in the first place. The effective pores may be in the neighborhood of tenths of microns, and so a small amount of electrolyte will flood it, and as you increase the state of charge, these pores open up by many factors, not just a 5 percent or a 10 percent, based on the state of charge.

As the pore volume increases, the amount of electrolyte, as Harvey showed, will effectively -- the total volume of liquid and solids will remain substantially the same but the quantity of electrolyte in the electrode will be a smaller fraction of the pore volume, and therefore, the overcharge pressure will decrease.

Now, you can then plot a curve of oxygen pressure versus state of charge that can be fairly steep for heavily loaded electrodes, but as you look at lightly loaded electrodes, the effect of state of charge is almost negligible, because the fraction change is so much smaller.

Now, one of the reasons that the oxygen pressure will decrease on burn-in is a redistribution of the active material, which increases the effective area of the negative electrode, and also the loss of electrolyte from the stack, as you have already described.

HENNIGAN: I think we can continue this discussion after lunch.

(Whereupon, at 1:00 p.m., the meeting was recessed, to reconvene at 1:45 p.m., the same day, in the same place.)

AFTERNOON SESSION   (2:00 p.m.)

HENNIGAN: I would like to call the afternoon session to order, please.

There were a few things that came up this morning that I thought I would comment on as far as our testing.

We had the oxygen electrode in all the cells we tested and among the group of polypropylene cells the only cell that would put out an appreciable signal for a charge control was the one that was in the cell with the Hercules separator, all the rest would not work. In fact, it was something like a 10, 20 millivolt swing.

I looked at the data for a while and I followed it very closely during the first 3000 cycles, but it was something on the order of 100 to 150 millivolt swing which would be good for a signal output.

The other thing, there was a statement made about the amount of electrolyte that we put in the cells. Nylon, which was a control, had 26; Hercules had 27; all the rest of the polypropylene had 24.

I haven't really looked at it too close, but if you will notice on those graphs I showed, we aren't putting that much less in the polypropylene separators, but they only have one-third to one-fifth the amount of electrolyte compared to the other materials.

On the next series of tests we will try to be more careful on these separators that we may not expect to work or to be on the dry side to come up with another method of adding electrolyte to the cells.

Now, of course, I would like to mention the purpose of this test was to get a separator that was comparable to nylon but, yet, was a polypropylene. We would like to have a material that you can fill a cell very easily and would not have to go through a lot of cycling and so forth.

There is quite a movement in NASA to reduce the price of spacecraft hardware. In the future it is going to be very difficult to add on costs to the costs we have now for cells. In fact, the trend is going to reduce that cost. So, we would like to come up with procedures that are very simple for the cell manufacturer. If we can eliminate some or at least keep them simple.

We have three more speakers this afternoon.
Mr. Stephenson, Mr. Dunlop from Comsat, and Steve Gaston
from Grumman. Mr. Stephenson, from Motorola, is the first
speaker. He is going to talk a little bit on what type of
separators they are investigating and some of the informa-
tion on their programs.

STEPHENSON: The Motorola usage of the nickel-
cadmium system is significantly different in the aerospace
industry. We are primarily concerned with small multi-
cell battery packs, usually in the order of about a half ampere
hour. However, what is of interest is, possibly, the test
procedures and the accelerated test procedures we do to
characterize these particular type cells.

Primarily what we are concerned with is rapid
charge cells normally in the order of charge rates of less
than one hour, specifically, the 1.2C rate.

In light testing these particular type cells we
normally charge them at the 1.2C rate to 40° Centigrade. We
use a temperature cutoff and discharge these cells at the
C rate and repeat this cycle every three hours. Now, you can
see this is a tremendously accelerated rate and the cells
never really have an opportunity to cool off, and normally
when these cells are cycled they run about 30 to 40 Centigrade
range.

Now, we repeat this cycle, as I said, every three
hours, 8 cycles a day, until the cell reaches 80 percent of
its rated capacity, which we designate as cell failure.

Normally, most of our vendor cells run anywhere
from 500 to 600 cycles before they reach 80 percent capacity
and usually 1000 cycles before complete cell failure, battery
failure.

We were unhappy with these cells because they didn't
give uniform temperature and rate capabilities through all the
temperature extremes. The batteries in which cells are
normally incorporated normally run anywhere from -30 to 60°
Centigrade in normal operation in a portable communication
system.

What we attempted to do was to stabilize the rate
capability of these cells throughout all of its temperature
ranges. We found that if we attempted to reduce the spacing
between the electrodes we could get better rate data, drain
data, drain rate at the lower temperatures. However, we were

very concerned with, if we used a thinner type separator what would this do as far as the cycle life of these batteries. So what we did, we assembled 288 cells, using a 2506 type separator, Pellon separator -- I should mention here that normally most of our cells either use a 2505 or two layers of a 2506 grade separator -- so we are effectively reducing the spacing between electrodes anywhere from about three to four-thousandths of an inch.

We started to cycle these cells. We made the thinner separator on this accelerated test routine that we have. The results that we got were rather surprising and, as yet, we haven't been able to figure out exactly why we got the results that we did.

As I mentioned, the normal cells that we cycle, using the thicker separator, have anywhere between 500 and 600 cycles to 80 percent of rated capacity. These cells, using the thinner separator, went anywhere from 900 to 1000 cycles to 80 percent of capacity, and we are still continuing the test until the cells fail completely. Out of these cells only one cell shorted and that was after 530 cycles.

We are just now starting to investigate why the increased life, using a thinner separator -- as you would believe that it would be just the other way around -- you would probably have cell failure very early in life rather than later in life.

We also investigated wetting agents at this accelerated rate and the effects of wetting agents are very pronounced on life. The separator that Pellon normally incorporates in their separator we looked at extensively and found that after only 20 or 30 cycles the batteries reached 80 percent of their rated capacity and 50 to 60 cycles complete failure of the battery.

So, we actively excluded any type of wetting agent in any of these batteries on the rapid charge routine and are again building new cells and reevaluating the data that we have, in an attempt to compare the thinner separator to the thicker separator.

Thank you.

HENNIGAN: Are there any questions for Mr. Stephenson?

PALMER: On that last point about the wetting agent,

I wasn't quite clear on what you were saying.

Did the thinner separators not have this wetting agent in?

STEPHENSON: Yes. We excluded any type of impurities in the separator itself.

PALMER: And your work was exclusively with nylon?

STEPHENSON: Yes. Right.

PALMER: Okay. Thank you.

RUBIN: I have two questions.

In your tests where you used a thin and a thick separator, was the actual electrode spacing different?

The second question is: did you change the quantity of electrolyte that you put in the cells?

STEPHENSON: Yes, to both of them.

As I said, we attempted to reduce the spacing and the entire reason for this test program was that we wanted to reduce the spacing between the electrodes.

As far as the amount of electrolyte, that was decreased with the thinner separator something about the order of 2.8 to 2.9cc per ampere hour, as opposed to the 2505 which only ran about 3.1cc per ampere hour. So it was reduced.

RUBIN: Do you use as a base of measurement the amount of ampere hours in the cell to determine the electrolyte fill?

STEPHENSON: At times we do. We use several techniques to determine the actual fill level and normally an increment type where we monitor the capacity and the pressure of the cell and determine what the probable level would be.

RUBIN: Thank you.

STEINHAUER: Did you failure analyze these cells, whether they failed due to, say, more rapidly with thicker electrolyte versus having the wetting agents in and so forth, or was it strictly electrical performance data?

STEPHENSON: You are asking me to speculate on why the cell failed. I purposely avoided this because we, ourselves, don't quite understand how the cells failed.

The normal failure mechanism for these cells is, say, three or 400 cycles on the cells with thicker separator. You can see a gradual increase in the end of charge voltage accompanied shortly thereafter by venting. This was also the failure mechanism on the cells with the thinner separator. However, it was an additional four or 500 cycles later.

CHARLIP: Did I hear you say spiral cells?

STEPHENSON: Yes. Small round cells, spiral wound.

CHARLIP: Could you define how you bonded or how you joined the can. What kind of bond did it have between the electrode and the can?

STEPHENSON: Between the electrode and the can? You mean, how we made electrical contact?

CHARLIP: Right.

STEPHENSON: With a welded tab on the plate.

CHARLIP: Okay. Thanks.

HALPERT: You said there was a wetting agent in the Pellon nylon. Did you put it in yourself, or was this put in by the Pellon people?

STEPHENSON: Both. We used as-received material. The designation, I think, is 2506-SK4, and we used a variety of different types of wetting agents, and we had similar results. All failure very early in life.

HENNIGAN: I would just like to ask one question.

Did you take out some wetting agents in some of these?

STEPHENSON: No, we didn't. We bought separator with and without wetting agents. We never attempted to remove it, although at times we did watch the separator to determine if there were any impurities incorporated in the separator as we received it.

HENNIGAN: I would just like to mention the
fact that lots of times these things come with what they
call a lubricant, which is the same thing as a wetting agent.

STEPHENSON: No, these are without a lubricant.

MAURER: Your description of the failure mode of
these cells is very similar to what we saw on long overcharge
with cells.   In that case the oxygen was consumed by oxida-
tion of the separator and the negative became fully charged
and cell vented.

Now, could that be happening here, in which the
negative gradually becomes fully charged cells vented because
of the high temperature that the cells are operating at,
and the difference between thin and thick separator, then, is
simply the difference in their areas?

STEPHENSON: The areas of what, now?

MAURER: Of the separator.   The thinner separator
has less area, therefore, less reaction takes longer to charge
the negative then.

STEPHENSON: As far as geometric, they are the
same amount.   Now the failure mode is exactly as you mentioned.
You can measure the charge on the negative and you see that it
has increased from what you put in there.   So, that is pre-
cisely what is happening.   Something is oxidizing, increasing
the negative charge up more fully, and it finally becomes
negative limiting.

MAURER: The geometric area of the separators is
the same, but their surface area must be different.

STEPHENSON: Yes, they would be.   There is less
material there.

HENNIGAN: Are there any more questions?

(No response.)

HENNIGAN: Thank you very much, Mr. Stephenson.

(Applause.)

HENNIGAN: We would like to go on to our next
speaker who also has some information on separators, determin-
ing the molecular weight of separator materials.

Jim Dunlop of Comsat.

DUNLOP: Thank you, Tom.

I am going to present some experimental results that we have on separator material from the Intelsat IV cells.

This data is taken from the real-life test program that we started back in 1969. We are using Intelsat IV cells which were taken directly from the production run and are being used currently in the Intelsat IV series satellites.

We have analyzed these cells electrochemically and chemically, periodically. We have saved the separator materials, and what I am going to show you today is the effect of the change in the separator material with time over about a two-and-one-half to three year period.

This separator is the non-woven nylon Pellon 2505.

(Slide 28.)

The samples that we used for determining the molecular weight distribution were taken after burn-in. That means after the normal cells were delivered and run through a 30 cycle acceptance test. After three eclipse periods and three storage periods that is one-and-a-half years of real-life testing. After four eclipse and four storage periods that is two-and-a-half years of real-life testing in the laboratory, and the total life of the cell at that time is probably around three-and-a-half years.

The molecular weight distribution and the average molecular weight values that are shown here were determined by jell permeation chromatography. This was done at Waters Associates.

What you see here is the average molecular weight. On a weight average basis it shows that initially the separator had an average molecular weight around 45,000 and after three eclipse seasons 31, and after four eclipse seasons 24,000. This data shows simply that the average molecular weight is decreasing with time.

(Slide 29.)

This r .de shows a normalized integral distribution for the nylon se₁ :ator, the function of the molecular weight.

Separator Sample	$\overline{Mw}$	$\overline{Mn}$	D.
After burn-in	45,000	i4,000	3.11
After 3 eclipse; 3 storage	31,000	7,200	4.35
After 4 eclipse; 4 storage	24,000	9,600	2.50

$\overline{Mw}$ = weight - average molecular weight

$\overline{Mn}$ = number - average molecular weight

$D = \dfrac{\overline{Mw}}{\overline{Mn}}$ "heterogeneity factor"

FIGURE 28

FIGURE 29

77A
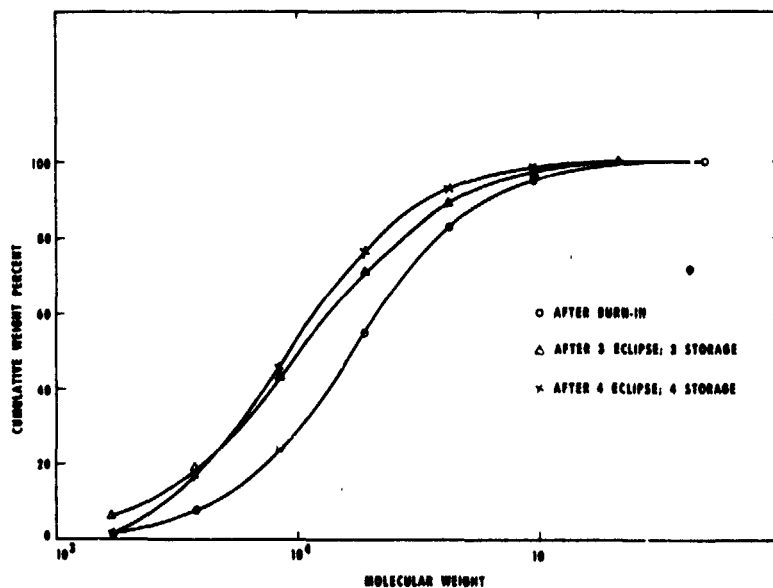
This is the accumulative weight percent starting here. The zeros here represent the separator after burning, and you can see that this has the higher molecular weights. After three eclipse seasons you shift back to here and after four you shift back to here, showing the average molecular weight distribution is shifting with time.

General comment is, that after four eclipse seasons approximately half of the higher molecular weight chains have been cracked.

That is all for the slides, please.

This data is somewhat qualitative in terms of evaluating the true effects of this on the separator performance, per se, but it definitely shows that the separator is soluble, the nylon separator is soluble at the time, and probably does augment the assumption made by Dr. Maurer that the solubility of the separator is not the weight limiting step in terms of the carbonate buildup in a nickel-cadmium cell with cycling.

Now, if you take this data, the quantitative aspects of this data, and couple it with the other information that we have determined from this test program, in essence, that there is a carbonate buildup with time associated with this test program, and that carbonate buildup seems to be fairly linear between one and two grams of carbonate per year, and that carbonate buildup that we previously presented, published before this conference and at the Atlantic City Power Sources Conference, can be directly related to this phenomena that was described last year by Dr. Maurer. That is, that the weight limiting step for the carbonate buildup is the electrochemical oxidation of the soluble byproducts of the nylon separator by the electrochemical oxidation at the positive electrode.

Of course, the problem here with the nylon separator is, that with time you can use this carbonate buildup to predict a failure, or you can actually measure it on an accelerated test basis as was done by Dr. Maurer.

We have used it in our program to predict the expected failure for a nickel-cadmium cell and the expected failure for the Intelsat IV cells, roughly about five to seven years with possibly, because of variations in the actual quality control or other aspects of the cell, we might drop this down to something like four years.

The experimental results that we are getting seem

to be justifying our expectations, and we will tak more about that tomorrow in terms of the test results, but this does bring out a point that I should make and, that is, there is a justification for getting rid of the nylon separator for long life satellite applications.

Now, I am not sure this morning exactly what the conclusion was for a six-month to a one-year to a two-year application, but it is very clear that for the seven to ten-year synchronous type application that there is no cell being currently designed today which really has the life expectancy of seven to ten years, if you are going to put a nylon type separator in that cell.

The other point that I would like to bring out, which I am not going to discuss today is, that we do have experimental evidence to indicate that there is a problem with the electrolyte redistribution depending upon the storage mode, and you certainly get a different result for continuous style charge mode than you do when you have an open circuit storage mode.

I think the other point that Tom Hennigan asked me to mention was, that we have been using Hercules separator material, which we obtained with his help, so one and one-half ounces per square meter in our nickel hydrogen cells that we have been running, and we have run this material over a year-and-a-half in the nickel hydrogen cell program, this particular Hercules material, and we have absolutely no problems that we have determined to date with that Hercules separator in that particular cell.

That 's for the ben of e people who might not be here tomorrow afternoon.

HENNIGAN: Any question.

STEINHAUER: Jim, I agree with your general conclusions. One thing, do you believe that this nylon is cracking in half or unzipping in monomer units?

DUNLOP: Monomer units. I don't really know exactly, but the distribution here just shows a shift in the average molecular distribution, so you can see how it looks. All this shows is that the longer chain lengths, 50 rcent of those have been cracked. The data is there.

STEINHAUER: Sure. The point that I am concerned with is, I agree with the oxygen getting tied up in this primary oxidation and oxidation of the degradation products. However,

it is difficult for me to consider more than just the --
when the primary oxid·:ion occurs you get carboxyllic acid
groups and those I can see going readily to carbonate. I
can't see all the carbon cr all the hydrogen being oxidized.
Therefore, is your carbonate buildup plate unloading, or is
it, indeed, attributable to the separator degradation?

DUNLOP: Well, Bob. I am going to answer that two
ways.

First of all, I believe that the results that you
are seeing here are due to separator. The reason I say that
is, that we have done this test for both cells, which were
open circuited and cells which are trickle charged, and if you
look at the amount of charging time or overcharging time for
those two modes, there is almost a two-to-one difference
between the amount of time that you are on charge with the
continuous trickle charge, to the amount of time that you are
on charge for the cells that are open circuit stand and then
periodically charged and then cycled. It turns out that there
is a pretty good correlation here between that overcharged
time and the carbonate buildup with time that is observed over
the three to four years.

What I am saying there is, we have observed about
one gram per year buildup in carbonate for cells that have
continuously been trickle charged. We have observed approxi-
mately half that much, or one-half a gram of carbonate buildup
per year for cells that have not been triple charged or open
circuited charged. So, it would lead you to believe that
that buildup is really coming from sizeable byproducts arriv-
ing at the positive electrode and being electrochemically
oxidized there during charging.

Now, the other point I would like to make here is,
that we do observe an initial carbonate level in all cells
regardless of how much trouble the various battery manufact-
urers take. That is similar between SAFT, between C.. ..·1
between Eagle-Picher. In all cases it represents ·. i..·
ficant amount. The same exact thing has been obsei ···· ·y
Battelle in their program at Wright-Patterson Air I ··· ·..·3.
It turns out to be something around 9 percent on a ·.. .·· ·
basis is carbonate in the potassium hydroxide.

I think this i. something that the battery manu-
facturers haven't been able to get out, probably due to the
positive electrode.

One thing that should probably be done in some of

these test programs, and I haven't heard anybody mention
it today, is, that if you are going to run these cells for
long periods of time with polypropylene separators, it
probably would be a good idea to check out your carbonate
buildup from time to time. I didn't hear anybody mention
that.

One of the arguments for using the polypropylene,
and it would answer directly your question is, that the poly-
propylene separator is not soluble in the KOH and would be
the rate limiting stuff.

STEINHAUER: I think Tom's data showed level car-
bonates admittedly, no extreme overcharge.

SCOTT: I don't remember the actual numbers for
the buildup that you were referring to, but what percentage
are they of this initial carbonate level of 9 percent or so?

DUNLOP: Rather than speak of percents, the ini-
tial carbonate level that we observed in the cells is around
six grams to seven grams, and the buildup is approximately
a half a gram to one gram per year.

SCOTT: Are you implying that starting out with
six grams that you are really worried about half or one addi-
tional gram or so?

DUNLOP: Yes, sir.

SCOTT: I think the thing we should be worried
about is that initial six grams. We have got to get that
out of there and then we can start worrying about something
else.

DUNLOP: No, sir. The answer to that question
is, that, first of all, the initial carbonate you observe has
to be coming from the plates. You can run a carbonate level
in a nickel-cadmium cell up to 50 percent or better of the
electrolyte, of a percent on a weight basis, and still run
the cell fairly well. You can go up to 75 percent if you
want to.

Now let me finish.

The carbonate buildup that you observe with time,
if it is due to an electrochemical oxidation, that means that
you are shifting the state of charge of your cadmium elec-
trode as you build up the carbonate, and in this particular

case we also showed a very nice correlation experimentally to an increase in the state of charge of the cadmium electrode, and this is directly at the expense of the overcharge protection.

That is what all this business has been about. It is what Maurer's paper was all about. It is what my paper has been about for two years, that carbonate buildup, if it is an oxidation phenomena coming by oxidation of the separator, means that you are shifting the state of charge of your cadmium electrode and eventually you don't have any overcharge protection, and so your cell fails, thereby becoming negative limited on charge. That is what the failure mechanism is.

There are two different mechanisms, that is the point.

SCOTT: I don't want you or anyone else to give the impression that we are not concerned with that initial level of carbonate in the cell, and that it may be a lot simpler to get that out of there to start with, than to solve the separator problem. I don't know.

But it seems to me that the data published now, well, the paper by the people from GE last year or so and some more recent results published by Battelle, indicate that you do start getting a significant problem at way lower than 50 percent carbonate in the electrolyte, especially, if you are talking about projecting these effects to seven to ten years.

I think we are already at the danger point right now from the residual carbonates in the plates. That is the only point that I would like to make.

DUNLOP: That is very true. Possibly, Dr. Font would like to comment on that. But we went to a fairly extensive program with SAFT to get the initial carbonate out and they went to the point where they vacuum sealed the electrodes, stored them in a bag in the vacuum, they assembled them in a facility which eliminates all the carbonate in the air, and when you get all done and you go to all these precautions the problem is, you co..e out with the cell in which the percent of carbonate in that particular cell is still just as high as the percent of carbonate in the ones that GE delivered.

All I am saying is, you can't decree this. You

better find out a way to do it. But you can't decree it just by going to very elaborate conditions.

STEINHAUER: There is a very easy way to keep the carbonate out of these cells. I saw it in the refractory metal industry. You simply fill the room with argon and put the processing people in with the diving suit.

(Laughter.)

HENNIGAN: We will move along now to the next speaker and, then, if there is any general discussion after the next speaker, we can go into that.

Thank you, Jim.

(Applause.)

HENNIGAN: I would like to mention here that, if after the next speaker anyone wants to give any results that we haven't heard from, why, feel free to do so. We will have to keep them short, though, because the other session we would like to hit about 3 o'clock anyway.

Our next speaker is Steve Gaston. I don't think I got around to asking Steve what he was going to talk about, but I know it is on separators.

GASTON: It is a short summary on screening tests which we conducted on the hundred ampere hour cell under contract NAS9-11074.

In this screening test we had built a total of 22 one-hundred ampere hour cells. Out of these 22 there were eight polypropylene cells and the balance were nylon cells, the nylon was P-2505.

The screening test consists of a test program which is shown in Table I.

(Slide 30.)

Before I got into the screening test program, I would like to mention that all cells were vacuum filled and the electrolyte amount was deficient. It was identical to the one in the nylon cells. I have a paper later which I want to go into details about the free volume determination which we did on these cells, and so we have assurances that the electrolyte quantity was sufficient.

In the test results we have first a number of
tests on the screening tests where we ran a number of differ-
ent cycles, including some capacity cycles, some high charge
cycles, some high discharge cycles, and we included an over-
charge cycle and orbital cycle.

Now, on the next curve I did not include the
orbital cycles as far as the capacity is concerned, because
they weren't full cycles, so they were omitted.

When we finished with 20° we repeated the same
test a 0°C.

(Slide 31.)

Plotted here is the positive electrode density.
The positive electrode density is defined as the positive
active material divided by the total electrode volume.

On the ordinate I have the positive electrode
active material utilization and that is in ampere hours gram
and for convenience it is 10^{-3}.

In the upper curve here it shows the 20°C data.
The upper curve presents the nylon P-2505. The W stands
for wash, all separators except the microfiber material was
washed three times in ethanol and followed by distilled
water wash.

The microfiber is relatively low in that, the
microfiber was not washed. It is relatively brittle material
and as the name implies, it is a very short fiber and very
difficult to handle.

Unfortunately, we didn't get the same success as
Tom Hennigan did on the 6 ampere hour cells. It is possibl
because the cell plate is relatively large. It is about
seven inches by five and one-eighths inch in area and it was
really difficult to handle.

At that time we said that we cannot handle it for
that large cell and we kind of put it aside. We still have
those cells and I would like to take another look at them
and see what caused the low performance. In fact, the 0°
data that we do later on it is even worse, it doesn't even
show up, it is below the lines. The results were not very
successful under ampere hour cells.

FIGURE 31

TABLE 1

100 A.H. CELL DEVELOPMENT TEST PROGRAM

TEST NUMBER	TEST STEP	AMBIENT TEMP. °C	CHARGE RATE AMP.	CHARGE VOLT VOLTS	DISCHARGE RATE AMP	DISCHARGE VOLT VOLTS
1.	CONDITIONING CYCLE	20	10.0	1.51	50.0	1.0
2.	3 CAPACITY CYCLES	20	30.0	1.51	50.0	1.0
3.	CAPACITY, HIGH RATE	20	30.0	1.51	100.0	1.0
4.	CAPACITY, HIGH CHARGE	20	60.0 *30.0	1.51 1.51	50.0	1.0
5.	CAPACITY, LOW CHARGE	20	15.0	1.51	50.0	1.0
6.	OVERCHARGE	20	30.0 for 8 hrs. *10.0 for 8 hrs.	1.51	50.0	1.0
7.	3 ORD. CYCLES (30% DOD)	20	37.4 for 58 min.		50.0 for 36 min.	

8.-14. REPEAT OF TEST NUMBERS 1.-7. at 0 C., EXCEPT CHARGE TO A FINAL VOLT OF 1.56 VOLTS, AND OVERCHARGE CURRENT FOR TEST NUMBER 13. IS 5.0 AMPERES INSTEAD OF 10.0 AMP. (TEST NUMBER 6.)

FIGURE 30

84A
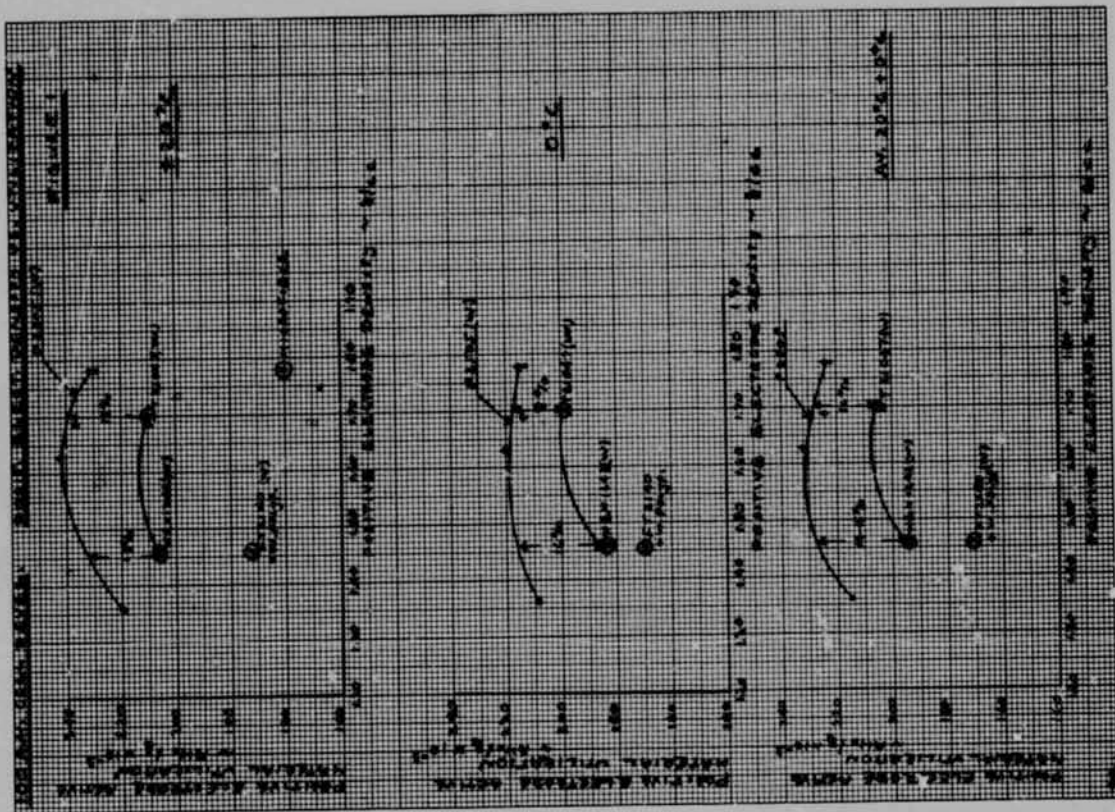
The T-21047 and the WX-1242 are about the same. They seem to follow the curve for the Pellon and we seem to be getting about a 12 percent difference. As a matter of fact, all of these electrodes, with the identical density, came from the same lot, so they are identical electrodes.

Again, here -- no, we don't have any of the same lot. I wanted to show the difference in density as far as the utilization is concerned.

In this case the WX performed somewhat better than the FT-2140, but what we did at that time, we used a combination of FT-2140 with a woven polypropylene, so it wouldn't be a fair test for the FT-2140.

I should have said that these are average values for all these tests which we conducted.

Now, the average values for $0°$ tests, and again we get about an 8 percent capacity loss for the polypropylene at a density of about 1.7 grams per cc, and it becomes more pronounced as we go to a lower density.

The third curve shows the average of them both. We just took the $0°$ and the $20°$ data and averaged them all out, and we get about a 10 percent lower capacity for the polypropylene about 1.7, and we get about 14 to 15 at lower density.

It seems that at a density of about 1.6 grams per cc this reaches a maximum.

Based on these results, at least on the 100 ampere hours, we have not seen an identical capacity performance. We have seen a lower capacity performance, but, of course, these are initial results.

I must add, we have done some initial testing but we did not want a prolonged experiment on these cells. This was just for comparison, it was an experiment test.

The hundred ampere hour cell, I would like to make one comment on the OAO cell which has flown on spacecraft A-2 and it has been flying for the last four years, and the batteries were built about a half year before, and they were built with nylon P-2505. I think at that time it was designated ML.

Although we have seen some degradation in the cell performance, it apparently -- what has been mentioned

before -- you can get maybe up to five years life with nylon provided you keep the temperature cool, which in A-2 it was around 55° to 65°F.

That is about all I have.

Are there any questions?

HENNIGAN: Are there any questions for Mr. Gaston?

(No response.)

HENNIGAN: Okay. Thank you very much.

(Applause.)

HENNIGAN: Are there any general questions that anybody would like to ask any of the speakers that we had this morning, or this afternoon, or does anybody have any other inputs they would like to put in their two-cents?

LACKNER: I would like to ask a question of Jim Dunlop.

On the cells that you were talking about earlier, what capacity were they, and what was the weight of the separator per cell?

DUNLOP: I can remember a couple.

The cells are rated 15 ampere hour cells. They are used at maximum depth of discharge of 60 percent. They are operated at a temperature approximately 68°F and cycles a little bit during eclipse operation lower and higher. It drops down to about 30°F and back up 30 in an eclipse day.

The separator weight, I believe, is 23 grams. Sixty ounces per square yard.

LACKNER: How many grams would there be in a cell?

DUNLOP: I think there is about 21 grams in a cell, Guy. I think that is the number that I remember.

LACKNER: Would the figure 2 grams per year change in that separator?

DUNLOP: It turns ou' that if you figure out that gram change, the weight change . pretty small. It is about a fifth the change in the ampere hour equivalent. I forget.

I think it is just about a tenth or two-tenths of a gram per year in the weight of the separator material for the amount of carbonate buildup that you are talking about.

LACKNER: What I am trying to figure is, if the carbonate buildup is strictly due to the separator, how much is the separator losing in weight?

DUNLOP: I think it is about two-tenths of a gram per year. We calculated it and, I think, the calculated number is about two-tenths of a gram per year.

The point I really chink is, that the weight change of the separator even for the one gram carbonate buildup per year isn't enough to make a significant change in the separator weight, the total separator weight. It is a fairly small percentage of the total separator weight.

LACKNER: It is just that, I seem to feel that if you attribute the carbonate strictly to the separator degradation, you would be losing an awful lot of separator.

DUNLOP: Like I say, it is about like one gram out of 23 in five years. It is a five percent change in the total separator weight, maybe in five years.

LACKNER: I think we, more or less, feel that we have to go on record every year telling you that we think it comes out of the plates. That's all.

(Laughter.)

HENNIGAN: We have another question.

COHN: On the same subject. I wonder whether any of the speakers, or anybody else here, would have an opinion as to what would happen to the life of nylon if we could essentially eliminate the presence of oxygen. Is it the oxygen that is causing it, or is it some other factor that is really causing the degradation?

HENNIGAN: Do any of the speakers have a comment on that?

RAMPEL : I will volunteer. I don't know why.

First of all, I feel the degradation of nylon is due to the exposure of KOH, to some extent. The hydrolysis in KOH, and of course it is a function of temperature and KOH concentration.

Secondly, I feel that the oxidation is due to the separator contact with the nickel oxides, particularly +3.

HENNIGAN: Dean Maurer also had a comment on your question.

MAURER: Guy and I disagree to some extent on that mechanism.

I agree that nylon is decomposed by hydrolysis independent of oxygen or anything else. Those hydrolysis products can be oxidized then by free oxygen in the cell, but in the paper I presented last year, I showed evidence that it was oxidized by the positive electrode itself. That is, the potential of the positive electrode allowed an electrochemical oxidation to take place and that caused a net oxygen loss.

That reaction will go on whether or not you have free oxygen in the cell. I suspect you are leading to proposing your negative limit in the cell, but even in that case you would have that oxidation.

RAMPEL : Dean, we have no disagreement at all. I did say that the separator was being oxidized in contact with the nickel oxides, particularly the +3 valences.

HENNIGAN: Jim Dunlop has a slide here which shows the reactions in the cell with the separator.

(Slide 32.)

DUNLOP: this is the one that was just described, which is the electrochemical oxidation, and this is the next reaction.

I think I really took this from the work that was done by Dr. McCallum   at Battelle. This is the one that he described in that paper where he described the various mechanisms by which you oxidize the separator. For this mechanism that we have shown here, which is the electrochemical oxidation at the positive electrode, the net reaction is, that for every gram of K_2CO_3 there is 1.16 ampere hours change in the state of charge on the cadmium electrode, if you assume that these reactions are correct.

STEINHAUER: I am glad you put that up, Jim.

$$6n\,(OH)^- + C_nH_{2n} \rightarrow n\,CO_2 + 4nH_2O + 6ne \tag{1}$$

$$3nCd\,(OH)_2 + 6ne \rightarrow 3nCd + 6n\,(OH)^- \tag{2}$$

$$3nCd\,(OH)_2 + C_nH_{2n} \xrightarrow{6ne} 3nCd + nCO_2 + 4nH_2O \tag{3}$$
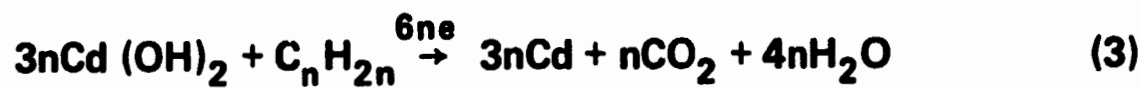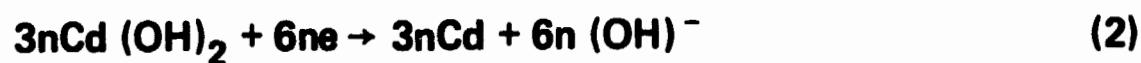
$$\frac{96500\ ahr}{3600\ equiv} \times \frac{6\ eq}{mole} \times \frac{1\ mole}{138.2g\ (K_2CO_3)} = 1.162\ \frac{Ahr}{g\ (K_2CO_3)}$$

FIGURE 32

This is the mechanism I would like to have kicked around here a little bit, because it is the one I disagree with.

Even in the primary oxidation, or in the degradation product, oxidation is all that carbon and all that hydrogen being oxidized, or are you only oxidizing amine groups after the primary degradation in carboxyylic acid groups? In other words, are you indeed tying up the amount of oxygen that that chemistry says?

MC CALLUM: It is my understanding that Dr. Reed made these measurements and he got very good correlation between the actual carbonate pickup and the number of extra ampere hours showing on the cadmium electrode.

DUNLOP: So did we. As best as you can do, we got a very good correlation, so we think there is a good experimental agreement. I have mentioned all this once before, but I will repeat it again.

SCOTT: John, did you just say agreement between the CO_2 and the amount of change in charged cadmium? That still doesn't answer Bob's question of how much of that total chain is actually split off and produced out of the original nylon structure. I think that is his question, if I understood it correctly.

If you only oxidize one carbon off the end of each of the two halves of the original molecule, you would have a very small fraction of CO_2 based on the original weight of separator material there, but the change in the cadmium could still be equivalent to that CO_2 and still be a very small amount compared with the total amount of separator present.

MC CALLUM: I don't think we had any evidence whether it went exactly as shown, or whether it is just one carbon off of a chain or the chain all the way. I don't think we have any evidence on that.

STEINHAUER: My point is, that if it is nylon 66, or are we just talking about two carbons and 12 that can be firm sealed, too?

HENNIGAN: Well, we can talk this over a little further at 6 o'clock at the cocktail hour, and I think that is where we will solve most of the problems.

There is one thing that came up in the sessions

this morning. We came over some c..ta, and I think I heard some others say something similar, if there is enough electrolyte in the separator the cadmium doesn't seem to grow throw. That might be an action item for next year, to find out why that happens, if it does.

I was going to bring up a couple of programs that went on about the middle of the '60s to determine why did zinc grow in a silver zinc cell, and both Yardney and Leesoma Moos did kind of similar work on it and they both came up with the conclusion that the zincate wasn't there in proper concentration. The zinc would tend to grow out and go look for it. I wonder if some similar type of thing isn't happening in our cells, that is not enough air, it keeps going out to look for some for it.

We don't have dendrites in these cells, it is more of a massive granular material that moves out. I am not saying it is similar, but it might be something we could think about over the next year for a topic then.

We are going to conclude our separator discussions here so that we can cover the next subject, processes and materials.

I am now going to turn it over to Jerry Halpert.

Thank you very much for your attention and help.
(For additional discussion see Wrotnowski on second day of workshop.)
(Applause.)
HALPERT: Thank you, Tom.

As part of our next session on materials and processes we will jump right into it and plan to have a break in a short time.

Our first subject, and when we talk about materials and processes we are talking about plaques, plates, anything other than separator at this particular time.

Our first speaker is Jim Bene from NASA/Langley. He is going to talk about sintering conditions and the quality of plaque materials.

BENE: Because there is a great deal of inquiries, questioning and wonder..ng about what Heliotek was doing on a contract with Langley, on a plaque contract, there was about an eleventh hour decision made to try to present a paper here

and to give people some idea of what is going on. The fellow
who was supposed to give the paper didn't come, and you know
who got the short straw about 2 o'clock this morning.

So, I am going to try to go through this thing
and, if you bear with me, it might be a little lumpy here and
there, but I think we can get through it, and hopefully we
will hear some comment on some of the things that we have
found.

The contract Langley has with Heliotek is a nickel
plaque study and the type things that we had hoped to gain
from that program is like what everybody else is trying to do,
they want all that good stuff.

We set out from a purely cosmetic standpoint not
to have any pits or pockmarks, such things as we have seen in
the past, or cracks in the sinter, no bubbles, and try to
reduce any agglomerations of the nickel powders.

We are also trying to keep a high porosity in the
plates and control that; get a very uniform pour distribu-
tion; control the thickness and do it uniformly; have a high
surface area within the plaque structure, and to obtain very
low electrical resistivity.

Now the thing that we are going to talk about is
a factorial experiment. It was performed not too long ago
and that had to deal with the experiment for the nickel
plaque as it would be used for a positive electrode.

The experiment was trying to evaluate the effects
primarily of sinteringtemperature, the resonant time at that
temperature, and composition of the forming atmosphere, and
it is all based on using a slurry production method.

(Slide 33.)

I am sure most of you people are familiar with
what we have here. It is merely a block diagram indicating
the slow process for production of a nickel plaque. We see
all the variables that are involved in trying to build the
thing, and all these variables end up, in some manner of
determining the quality of the plaque you have an end product.
Some of the most critical ones thit we feel that we found is
the composition of slurry, the blade separation, obviously,
and the temperature resonant time and the forming gas compo-
sition during the sintering process.

For this factorial experiment we fixed all the variables up to the sintering point and those variables that were fixed were determined during a trial and error process to make a nickel plaque for a positive electrode. It was those variables we felt that gave us what we considered a fairly good plaque.

(Slide 34.)

The variables that we fixed, that are here, was the nickel slurry, the nickel grid, and the slurry applicator, and the drying time, or the drying procedure.

Nickel slurry probably doesn't vary too much from what most other people use, and the mixing procedure is probably a little different in that we use a very slow tumble rate to do the mixing for a very long period of time. This not only gives us fairly good mixing, but a o de-aerates the slurry.

Nickel grid is 3 mil as you can see there. It is cleaned with ammonia, I think it is hot ammonia, an acetone bath. Is that correct?

VOICE: Hydrogen peroxide.

BENE: Also, the nickel grid tends to have a cupping effect where it has been punched, and it is also stretched to stretch the border areas, to match that of the perforated areas, to get rid of buckling, so that you have a much flatter plaque when you are finished.

The slurry application ductile blades that have sintering fingers that are dovetailed prior to entry into the ductile blade, and the drying is done at room ambient.

(Slide 35.)

Now, here are the variables during the factorial tests. Now, the base level in the furnace, and the furnace is a three-zone furnace, and as you see here the base level is selected at 775, 925 and 1000°C, and the belt speed 6 inches per minute and about a 20 percent hydrogen in the forming gas. The forming gas rate was fixed at 140 cubic feet per hour, I believe, if I remember right.

The numbers for the base level, again, were determined apparently during the test program and these were the numbers we found that gave us what we considered a

fairly good plaque and very close to the parameters that we desired for the positive plaque.

The unit variable that we chose here for this experiment was plus or minus 25°C for all temperature zones, plus or minus 2 inches per minute for belt speed and 10 percent variation in the hydrogen forming gas. All total in the base run and the factorial run give us a total of nine runs of sinter.

(Slide 36.)

Here we have a plot of the temperature profile within the oven. It was obtained by imbedding thermocouples in a piece of plaque material and allowed to go through the furnace.

(Slide 37.)

Now, after all the plaque samples for the experiment were sintered, all the plaque was tested and evaluated for properties shown here. Void volume thickness, mechanical strength surface area, electrical resistivity in the unloading. Two other things were appearance and good location.

Now, appearance kind of fell out because all the plaque was blemish-free, we had no bubbles, no pockmarks, no cracks, and the grid location was sintered in all samples we looked at. No point in including that here.

The void volume was determined by using the weight of the water imbibed by vacuum impregnation in the samples. Sample size, about 2-3/4 by 3-1/4, and we obtained something like 2 percent reproducibility. Thicknesses by standard micrometer measurements and it was used about five readings taken on each plaque sample, and the variable there was plus or minus five-one-hundredths.

The mechanical strength, there, again, was a little different. What we used was, more or less, a hardness tester to determine the amount of crunch or crunch-up that you get in the sinter itself, so that actually the smaller the number you get, the more hard the sinter is.

Surface area was determined by double layer capacitance potentiatic step, wherein the sample is biased to a negative .5 to .9 volts as read by a nickel oxy-hydroxide reference electrode and the pulse was 5 to 50 millivolts for about 100 milliseconds. The double layer capacitance was
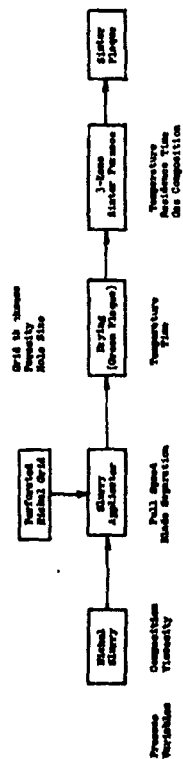
FIGURE 33

FIGURE 34

	Furnace Setpoints	Belt Speed	% Hydrogen in Forming Gas
Base Level	775-985-1000°C	6 in/min	20%
Unit	25°C	2 in/min	10%
High Level (H)	800-950-1025°C	4 in/min	30%
Low Level (L)	750-900-975°C	8 in/min	10%

Run			
1	L	L	L
2	L	H	L
3	L	M	M
4	H	L	H
5	M	M	M
6	H	M	M
7	M	H	M
8	H	M	L
9	Base	Base	Base

FIGURE 35

FIGURE 36

93A

charged at about 10 milliseconds for all samples.

BET was going to be run by Goddard. I understand they ran into a problem and as yet it has not been done.

Electrical resistivity would run around 3 inch by 1 inch samples where a 5 amp current was passed through sample and the voltage drop measured on a fixed spacing.

The impregnation was just by standard aqueous nickel nitrate loading and 6 percent cobalt. The samples were dried at 120°, and there were five impregnations.

(Slide 38.)

Here we have got a real busy one. This is all the data that was obtained during the experiment.

Now, all of the parameters that were checked were performed on at least three samples for each run, except for the double air capacitance, which is only two samples.

I think one of the things you see here in general is, that all the plaque that was acceptable from the standpoint of the thickness, the porosity, the mechanical strength, electrical resistivity, and the weight gain. As you might expect, the higher the temperature -- I don't know if you people can follow me as I am going over this thing -- you will notice that the lower the temperature or the higher the temperature the plaque thickness is thicker for the lower temperature and thinner for the higher temperature, and by the same token the mechanical strength is much stronger for the higher temperatures. You will find the electrical resistivity is even lower for the higher temperature. That type thing you expect to see.

The double layer capacitance we measured here is about the same as what we found on a commercially available plaque. It was made from a slurry process and about twice as high as what we found on commercially available plaques made from a dry powder. Resistivity-wise the average we obtained here is about, oh, turn it around, the commercial plaque made from a slurry was about 1.3 times higher than that made from a dry powder which was 1.9 times higher.

There is not much to pick and choose from in the weight gain and from the impregnation.

If you will notice, most all of these numbers are

small. There is very little variability in any of this.

We are going to try to determine what effect all
these different factorial runs had on one another by what
they call a student T test to the data, which is a statis-
tical method to determine or to establish the variability --
oh, boy, I am out of my league on statistics. Anyway, it is
a student T test.

You take the numbers and what you determine is
the variability of the number from the average mean, and
using that number you calculate a T value which is given
to you, a formula out of a handbook.

(Slide 39.)

What you arrive at, anyway, when you are looking
at the deviation from the mean average and use that to cal-
culate T number, and if you come up with a number and if this
number is larger or greater than T, it is greater than the
number you get out of the handbook, and then you say that
the test indicated a significant difference. If it is
smaller, it is the same.

We apply this to all the different variables we
had there and six rate different runs.

Just a typical example there for the plaque thick-
ness.

(Slide 40.)

Here we have the mean average values of all the
plaque properties that function as a sintering condition and
the results of that application is the T tests.

I want to emphasize that the belt speed apparently
didn't have any effect during this experiment on any of the
plaque properties that we looked at. Apparently the belt
speed was slow enough that we got sufficient sintering even
at the higher belt speed. What you might expect, too, at
the higher temperatures we get the difference in the thick-
ness and we get higher mechanical strength and a lower elec-
trical resistivity. With the hydrogen we get a higher void
volume and a thicker plaque.

What we learned from this, I think, is that the
base conditions that we chose were pretty well right on the
money, because the variations we got here are pretty small.

Table 3. Test Methods for the Evaluation of Plaque Properties

Plaque Property	Test Method
Void Volume	... of water imbibed
Thickness	Micrometer
Mechanical Strength	Displacement Device
Surface Area	Double Layer Capacitance by a Potentiostatic Step / NT
Electrical Resistivity	Four Point Probes DC Measurements
Impregnation Loading	Standard Procedure, Weight

FIGURE 37

Table 4. Summary of Data and Results of the Factorial Tests

FIGURE 38

$$t_i = \frac{|\bar{x}_i - \bar{x}|}{\bar{s}(n)\sqrt{\frac{1}{n_1} + \frac{1}{n_2}}}$$

$$\bar{s}(n) = \sqrt{\frac{s_1^2 + s_2^2}{n_1 + n_2 - 2}}$$

where $\bar{x}_i$: Mean of distribution i
n_i: Number of samples in group i
$\bar{s}(n)$: Pooled estimate of s

$$\bar{x}_i = \sum_i (x_i - \bar{x}_i)$$

FIGURE 39

Table 5. Mean Average Values of Plaque Properties as A Function of Sintering Conditions and the Results of Student "t" Tests

	Temperature			Belt Speed			% Hydrogen		
	High	Low	"t" Test	High	Low	"t" Test	High	Low	"t" Test
Void Volume (cm³/in²)	0.268	0.271	Same	0.263	0.277	Same	0.279	0.261	Different
Thickness (mils)	23.2	24.4	Different	23.8	23.9	Same	24.4	23.3	Different
Mechanical Strength	8.2	9.3	Different	8.6	8.9	Same	9.0	8.6	Same
Normalized DLC (m²/cm²)	1.54	1.60	Same	1.59	1.55	Same	1.58	1.56	Same
Elect. Resistivity (10⁵ ohm cm)	7.1	8.1	Different	7.5	7.7	Same	7.7	7.5	Same
Impregnation Loading (g Ni(OH)₂/cm³ voids)	1.91	2.02	Same	1.95	1.98	Same	1.99	1.94	Same

FIGURE 40

If you look at the base numbers that we had for the porosity or the void volume, and the thickness are going off a little bit and, if we adjusted the ductile blade, we can bring the thickness up to a desired level of 25 mils, we would only be about 2 percent off from what we consider the desirable void volume within that sinter.

I guess we can say, then, that the test was useful. It showed that the process for the positive electrodes, which was the 9 base level, was acceptable from a standpoint of plaque, and also indicated how we could go about making plaque for the negative which we want to be a little bit more porous, and also indicated the effects of temperature on the plaque structure and the effect of the hydrogen flow. Obviously, if you want to see some difference in belt speed, we would have to speed it up much faster and reduce the residence time in the furnace.

That is about it.

HALPERT: Any questions?

GROSS: Could you repeat what you said, Jim, about the electrical resistivity. You made a comparison between the data that you had and about plates made by a dry powdered method.

BENE: Right. We compared the plaque that we made and a commercially available plaque that is produced in much the same manner. It is a wet slurry process. We also compared it to a commercially available plaque that is produced by the dry powder process.

The commercial plaque by the wet slurry process had a resistivity that ran about 1.3 times as high, and that from the dry powder was 1.9 times.

GROSS: Your resistance was lower then?

BENE: Lower, correct.

GROSS: What percentage of the conduction was attributed to the grid?

BENE: That is a real good question.

SEIGER: One-third. I happen to remember some of the numbers. The nickel grid gave us a voltage drop of

about 30 millivolts, whereas an entire sinter on the grid, that combination gave us a voltage drop of 13 millivolts.

BENE: Was that the question you asked, Sid?

GROSS: Yes, that was the question.

BENE: I misinterpreted your question then. I was trying to answer something else.

GROSS: I would like to ask if there is anybody who has run any tests on the electrical conduction in the direction of thickness of the plaque. We have done this and have gotten some surprisingly low values. If there is, I would sure like them to contact me sometime or speak up now.

CHARLIP: Jim, in your first slide you were talking about 59.6 percent, I think, nickel 287, 2 percent binder, methyl alcohol 7.4 percent, the ionized water 34.2 percent. You had a pore former .8 percent. Is that a fugitive? Is that something that burns out?

BENE: Right.

CHARLIP: Would you care to elaborate on that pore former, please.

BENE: It gases off during the sinter process.

CHARLIP: I know, but would you elaborate on what this material was, what is a pour former?

Oximide.

CHARLIP: Oximide?

Thank you.

HALPERT: Okay. Thank you, Jim.

(Applause.)

HALPERT: Our next speaker will now discuss some of the work that was performed on one of the NASA programs involving comparison of the chemical, electrochemical and high temperature electrochemical impregnation process.

Gerhard Holleck from Tyco will discuss that work.

HOLLECK: With support from the NASA/Goddard Space Flight Center we have carried out a study with the aim of developing uniform and predictable battery plate for nickel-cadmium aerospace cells.

The experimental approach involved the preparation of porous nickel plaque and the measurement of its physical characteristics to test for uniformity.

The impregnation of porous plaque with nickel or cadmium hydroxide to form positive and negative plates and the testing and characterization of the plates to define the influence of manufacturing and operating variables.

The result of the first two tasks have already been discussed in earlier meetings. Today I will report on a factorially designed experiment aimed at illuminating in a comparative study the effect of plaque preparation, plaque thickness, impregnation process and loading level with active material.

In evaluating the results, the separation of the treatment comparison with the main effects and interactions is a convenient and powerful method of analogcus, especially in cases where interactions are small relative to main effects.

In our case, as will be seen later, in directions we often found large relative to main effects and this demonstrates further the complexities of the problem.

(Slide 41.)

This shows the basic setup of the experiment. The plaque type was investigated at three levels, dry sinter plaque, slurry-coated plaque on nickel screen and a slurry-coated plaque on a perforated sheer substrate.

The plaque thickness on two levels, the thin and the thick plaque, was normally 20 and 30 mils. Then three levels of impregnation method, chemical conversion, electrochemical conversion and the high temperature electrochemical impregnation. Again, this was investigated as two loading levels of normally 5 and 8 ampere hours per cubic inch.

The test was a 30-60 minute cycle with 25 percent depth of discharge and 5 percent overcharge.

The nickel plaques were prepared by slurry-coating and by loose sinter powder layoffs with the substrate sintered. The nickel powder was Ingot 287. The green plaques were sintered in hydrogen atmosphere at 903C for 30 minutes for the slurry cultured plaques and two times 20 minutes for the dry layouts.

The final plaque was characterized by measuring thickness and porosity, electric resistivity, and mechanical strength in a four point band test.

(Slide 42.)

This slide shows some average values of the plaque. The sinter porosity -- and these are values, porosity values, corrected for the substrate value, mechanical strength and resistivity.

You see the loose sinter powder sinter are slightly higher in porosity than the slurry-coated materials. Please disregard this. That is not real. It comes from an error in thickness measurement due to the screen structure on the surface of the plaque. Mechanical strengths and resistivity correlate quite well with the average porosity. These are average values.

(Slide 43.)

This shows you the conditions of the impregnation process. The chemical conversion process was vacuum impregnation with saturated nickel nitrate or cadmium nitrate solution followed by drying and then conversion in 25 percent KOH at 80° for 70 minutes. Plaques were then washed, dried and weighed and the process repeated.

The electrochemical conversion started out with the same step but then the plaque was directly transferred into KOH with a cathodic polarization and a current of 150 million ampere per square centimeter.

The high temperature electrochemical impregnation was carried out in a solution containing .3 molar sodium nitrate and 2 molar of nickel nitrate or cadmium nitrate.

The temperature was approximately 104°. It was a boiling solution and the pH was adjusted before heating the solution.

Positive plates were impregnated at a half amp

per square inch and negative plates at a quarter of an amp.

(Slide 44.)

This shows the basic steps of the test procedure. The plates were formed at a C over 2 rate with 100 percent overcharge up to a constant capacity. Then the initial capacity before the test was determined at a C over 2 rate of 100 percent overcharge. Then hundred test cycles with 60 minutes charge, 30 minutes discharge and 25 percent depth of discharge at room temperature were carried out.

The starting was at 80 percent state of charge for negative plates and at a full charge for positive plates.

During the cycling charge and discharge potentials were recorded. After the last regular charge a complete discharge was carried out and after this the cell was fully charged with 100 percent overcharge and, again, fully discharged.

(Slide 45.)

This shows you a typical example of potential time curves obtained at positive plates. The shape of the test cycle did not change during the hundred cycle. It was practically identical at the beginning and at the end of cycling.

Upon full discharge, this is the next cycle, you see a potential variation at the point where the regular cycle ended and upon full charge after this with overcharge. That actually continues further than the one I have here.

You see a slight change in the potential time behavior at the point where the regular charge would have ended the cycle. Even after 100 percent overcharge the following complete discharge shows some structuring in the potential.

Now, if we assume that the end of discharge is a common point and, I think that it is safe to do so, we can line up the second and the fourth graphs of these two curves, and that is done in the next vugraph.

(Slide 46.)

So, here it becomes quite obvious that the electrode is actually cycling in this case between approximately

FACTORIAL DESIGN FOR MANUFACTURING VARIABLES

A (plaque type) at three levels

    A_0 - dry sinter plaque (D)
    A_1 - slurry-coated plaque, Ni screen substrate (S)
    A_2 - slurry-coated plaque, perforated sheet substrate (P)

B (plaque thickness) at two levels

    B_0 - thin plaque (20 mils)
    B_1 - thick plaque (30 mils)

C (impregnation method) at three levels

    C_0 - Chemical conversion
    C_1 - Electrochemical conversion
    C_2 - High temperature electrochemical impregnation

D (loading level) at two levels

    D_0 - low loading with active material (5 Ahr/in.^{3})
    D_1 - high loading with active material (8 Ahr/in.^{3})

Test: Simulated near-earth orbit 30 min discharge
                                   60 min charge
                                   25% depth of discharge
                                   5% overcharge

FIGURE 41

PLAQUE IMPREGNATION

Chemical Conversion:

    Vacuum impregnation – saturated $Ni(NO_3)_2$
                       or $Cd(NO_3)_2$

    Dried (80°C)

    Conversion – 25% KOH, 80°C, 30 min

    Washed; dried; weighed

Electrochemical Conversion:

    Vacuum impregnation – saturated $Ni(NO_3)_2$
                       or $Cd(NO_3)_2$

    Conversion – 25% KOH, 80°C, Cathodic 150 mA/cm^2 30 min

    Washed; dried; weighed

High Temperature Electrochemical Impregnation:

    Solution: 0.3 M $NaNO_3$ + 2 M $Ni(NO_3)_2$ or $Cd(NO_3)_2$

    ~104°C (boiling), pH 4

    Positive plates – 0.5 A in.^{2}

    Negative plates – 0.25 A in.^{2}

FIGURE 43

Average Values for Plaque Porosity, Mechanical Strength, and Resistivity

Plaque		Sinter Porosity (%)	Mechanical Strength (kg/cm^2)	Sinter Resistivity $\Omega \cdot cm \times 10^{-4}$
Loose sinter	thin	81.4	60.5	2.4
	thick	81.8	66.6	1.9
Slurry on screen	thin	82.6	91.1	1.7
	thick	79.0	96.6	1.5
Slurry on perforated sheet	thin	79.6	80.8	1.6
	thick	79.4	102.7	1.4

FIGURE 42

TEST PROCEDURE

Formation (C/3, 100% overcharge, 30% KOH, to constant capacity)

Initial Capacity (C/3 after 100% overcharge, 30% KOH)

100 Test Cycles (60/30 min, 25% depth, 5% overcharge, 30% KOH, room temperature, starting with discharge from 80% state-of-charge for negatives and 100% charged for positives)

Charge and discharge potential recorded during cycling

After last charge, complete discharge (0.8 V cell)

Full charge (100% overcharge), full discharge

FIGURE 44

50, between these in the regular cycle. But despite this cycling at the low end of the full capacity it is remarkable that the potential time behavior is very similar to the starting potential time behavior of such a curve.

The reason for the shift from the full 100 percent state of charge to the lower end or center portion of the state full charge is the oxygen evolution which is a periodic reaction and increases with the state of charge. Obviously, the amount of overcharge was not sufficient to keep the electrodes in a full charge state.

An average positive electrode cycle at the end of the hundred cycles approximately between 35 and 65 percent, between these limits which are given up here, so in this respect this is somewhat of an extreme case here.

We have also carried out quantitative measurements of oxygen evolution as a function of state of charge in connection with our work on negative limited nickel-cadmium cells and I will report on those results tomorrow.

(Slide 47.)

This vugraph shows the analog cycle for negative electrodes. Here no special memory effects were observed. So there is not really very much to say about these curves.

Before I discuss the capacity changes during the test cycling, I want to make a few comments regarding the data evaluation.

We used Yates procedure for two level factorials and analyzed the data in four factor blocks. This is illustrated in the next vugraph. One such four factor block would be the shaded area, for example, and there are nine such combinations which we can make to carry out with this data.

The analysis was carried out for 95 and 80 percent confidence limits. The level of significance was determined by assuming that third and higher order interactions are nonexistent and that the variance in these terms is due to error. This gives us a conservative confidence limit, since some third order interactions might well be real.

(Slide 48.)

This vugraph shows a table giving the capacity retained of positive electrodes during the hundred test cycles.
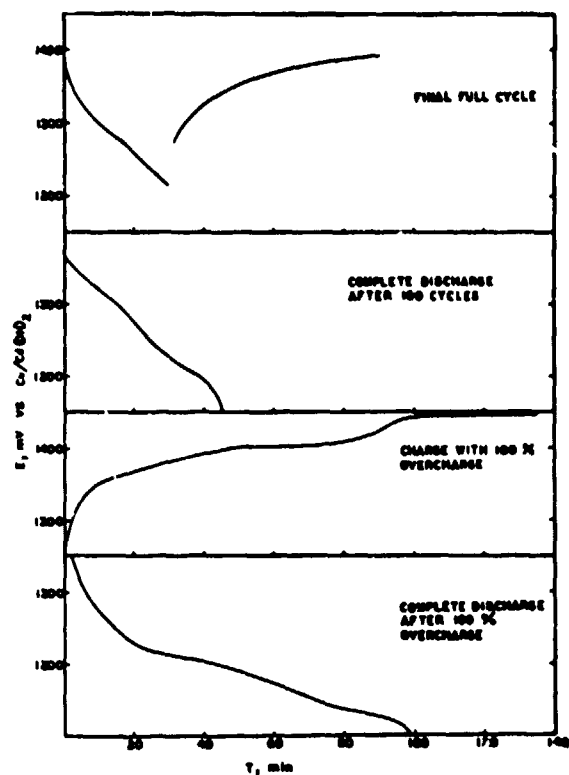
FIGURE 45
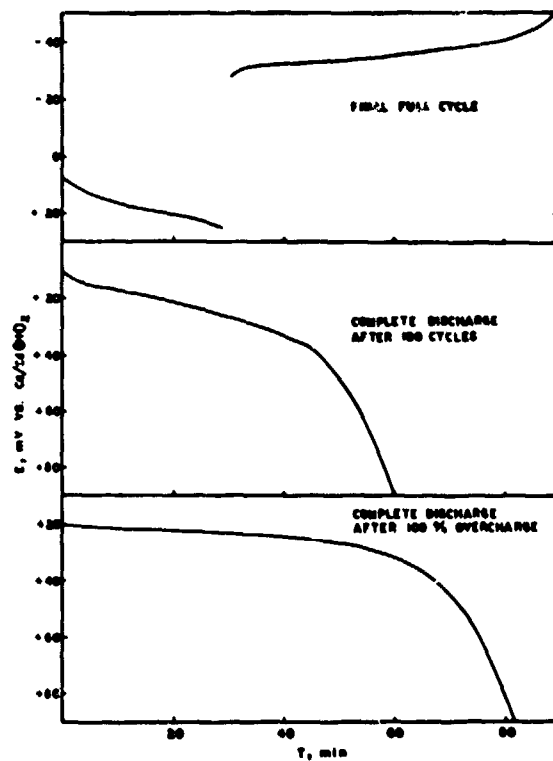
FIGURE 47
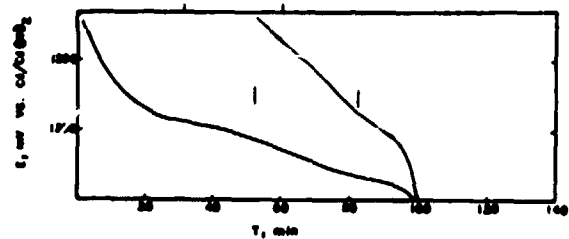
FIGURE 46

		Loose Sinter		Slurry Screen		Slurry Perforated Substrate	
		Thin	Thick	Thin	Thick	Thin	Thick
Chemical Conversion	Low	90	90		82.5	100	100
	High	93	90.5		90		91
Electrochemical Conversion	Low	96	97	100	90.5		114.5
	High	96	100.5	101.5	90		93.5
HT Electrochem. Impregnation	Low	87.5	98	90.5	78.5	86.5	83.5
	High	93.5	101	94.5	86.5	90	87.5

Positive Plates – Capacity Retained After 100 Test Cycles

FIGURE 48

101A

The overall changes are relatively small and in average they are about 5 percent loss of capacity during the cycle regime.

From this data it would appear that the plaques impregnated, especially the slurry-coated plaque;, impregnated by the high temperature electrochemical impregnation process performed less favorably than the equivalent plaques impregnated by either one of the conversion processes.

This should, however, not be attributed to the high temperature electrochemical impregnation process as such. For example, if you compare the loose sinter plaques you find practically identical performance in all impregnation procedures.

Why, then, do we find this difference between the loose sinter plaque and the slurry-coated plaque in the high temperature electrochemical impregnation, whereas the other impregnation methods were practically insensitive to the plaque structure or, if anything, improved when you go from the loose sinter to the slurry-coated materials.

The high temperature electrochemical impregnation method depends on a balance of a number of different diffusion processes and that the plaque and impregnation parameters have to be matched to obtain optimum results.

Since we have not had time to determine the optimum conditions for each plaque we use a standard procedure to determine primarily for loose sinter plaques in all cases.

I might mention that continuing work for NASA/ Goddard carried out in our laboratory by Ed Rubin, where the structure of slurry-coated plaques was modified, resulted in excellent plaques.

The factorial evaluation shows practically no other main effects. There are, however, significant interactions.

Now let me quickly backtrack and recall what this means.

(Slide 49.)

For example, if we look here, just at the curve, the response of the levels of B zero and B 1 here, effect a change in level of factor A is a response to a change in the level of factor A is here independent of the variable B.

Thus we have no interactions. However, if we look now, let's say, at B zero and B 2 a change in the level of A from, let's say, zero state, ground state, to 1, does cause a different response.

Now, if we use the average value as it is done in the Yates evaluation we will find no response whatsoever. However, in truth it is not no response, but it is a reverse response on the two levels of B.

(Slide 50.)

For our specific case I have indicated two such cases here. For example, the chemically impregnated slurry-coated perforated substrate plaque performed better than the loose sinter. The opposite was the high temperature electro-chemical impregnation. Interaction was also observed between loading level and plaque thickness. An example is shown here.

It shows that at the low loading level the thin plaque performed better and at the high loading level the thick plaque was more favorable. This is a comparison which is indicated on the bottom of the slide. This is comparing the electrochemical conversion and high temperature electro-chemical impregnation. The dry sinter and slurry-coated that was on the big layout, the lower left corner.

(Slide 51.)

This shows the results of negative plates. Here the changes in capacity during the hundred test cycle were considerably larger. They were on the average of 15 percent. Maybe you can put the overlay on here.

These are average values of these columns here.

The most striking result in this comparison is that the high temperature electrochemical impregnation behaved much better in this test, resulted in much better cadmium electrodes, than the electrochemical or chemical conversion processes.

This may reflect a better distribution of the active materials in the plaque structure.

Other results of interest are the lower load plaque retains larger fractions of its capacity. This holds throughout all impregnations.
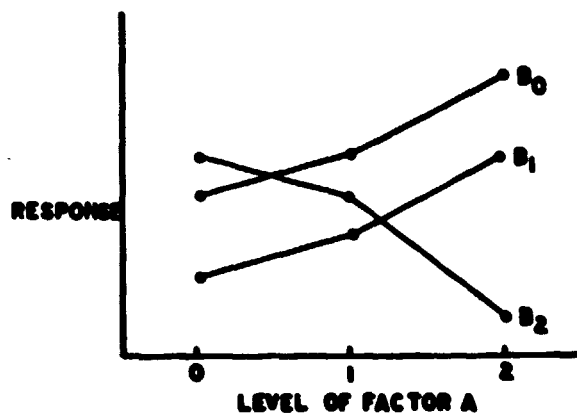
FIGURE 49

	Loose Sinter	Slurry Perf. Sheet
Chemical Conversion	94.8	100
H.T. Electro Impreg.	93.3	86.4

		plaque	
		thin	thick
Loading	low	97	88.7
	high	95.9	97.7

Electrochem. Conv , H.T.E. Impreg. / D , S

FIGURE 50

Negative Plates — Capacity Retained After 100 Test Cycles

FIGURE 51

Here, too, significant interactions were observed, especially between impregnation methods and plaque-type or plaque thickness. For example, of the plate prepared by chemical conversion the slurry-coated perforated sheet was considerably superior to the loose sinter, if you compare these two, whereas if you compare, for example, the analog values for the high temperature impregnation method you find practically no difference between the two plaques.

Based on those results we may draw the following conclusions:

Acceptable positive plates can be obtained by any of the three impregnation processes on any of the plaques investigated.

Of the three methods, the high temperature electro-chemical impregnation process depends on the largest number of variables. If they are properly determined and regulated, this process may allow the closest control over the disposition of active material.

Also, weakening of the plaque structure due to corrosion is considerably less than with the conventional impregnation methods.

Of great practical importance is that plaques can be impregnated in a one-step process.

The performance of negative plates appears to be much more dependent on manufacturing variables.

Negative plates prepared by the high temperature electrochemical impregnation process show a significantly more favorable capacity retention than those prepared by either of the two conversion processes. This reflects pro-bably a more uniform distribution of active material through-out the plaque structure. The plaque structure, also, is of importance.

The slurry-coated plaque without any negative was less capacity change.

Further, the less heavily loaded negatives retained a larger fraction of their capacity.

Thank you.

HALPERT: Thank you, Gerhard.

Are there any questions or comments regarding this?

SCOTT: What is your justification for superimposing those two positive electrode discharge curves at the right-hand end, rather than anyplace else on the curve and essentially calling that a hundred percent discharged? I assume that is what that implies.

HOLLECK: Yes.

SCOTT: I don't understand that analysis.

HOLLECK: Well, even if it is not exactly a hundred percent, I think you can assume if you discharge the electrode to a low potential that you have a very highly discharged electrode, and that that is the closest of a common point you can get on these curves.

SCOTT: Did you do any associated chemical analysis for residual charge negative material to confirm that analysis?

HOLLECK: Not on these tests here.

GROSS: Do I understand your charts correctly, that you are showing percentages of the initial capacity? You showed the capacity on those charts at the end of a hundred cycle relative to the initial capacity, is that correct?

HOLLECK: Yes. That is the measured capacity at the beginning of the hundred cycles. It is not theoretical capacity.

GROSS: Okay, that is the measure at the beginning.

Do you show, also, capacity at the end of the hundred cycles?

HOLLECK: These values which I showed, these percentage values, were percent of capacity retained, so that means if there was a value, let's say, of 95 percent, that means the electrode lost 5 percent of the capacity it had at the beginning of the hundred test cycle. Both measured by full discharge at the C over 2 rate after overcharge.

SULKES: Could you make some comment on the actual utilizations you got from the various processes?

HOLLECK: Yes. We have also looked at the values

relative to the theoretical capacity and the positive
electrodes, the theoretical capacity and the actual delivered
capacity is very close. On the negative electrodes we find
a larger discrepancy and the end values after the hundred
cycles compared to the theoretical capacity calculated by
weight gain of nickel electrodes is approximately 90 percent
and of the cadmium electrodes it is approximately, I think,
between 50 and 70 percent.

GROSS: The only thing is, do you have numbers
such as ampere hours per cubic inch, because 90 percent of
nothing is still nothing. Are there actual 6 ampere hour
per cubic inch, 7 ampere hour per cubic inch for each pro-
cess?

HOLLECK: Oh, yes. We measured ampere hours per
cubic inch. I cannot really give you now a specific number
of this. But, yes, they are in the report.

HALPERT: Thank you, Gerhard.

(Applause.)

HALPERT: Two points I would like to mention at
this time. We have that list. I have now been returned the
list of names. If you have not signed it, please see me
during the break.

The second item is, all those who have presented
information here we would like to have copies of your vugraphs
for inclusion in the report, and we would appreciate it, if
you brought them with you, we will take them -oday.

Tom Hennigan will take all those in the separator
section, and I will take all those in the materials group.

The survey that Floyd passed around today, we
would like to have the results this afternoon for tabulation,
so that we can present them to you tomorrow. So, if you have
some time during the break, if you just scratch down your
results or your information, we would appreciate it.

We will take about a fifteen minute break and be
back here at about 4 o'clock.

(Recess.)

HALPERT: Our next speaker for this afternoon has
done some work on the high temperature electrochemical process

and is involved with a new step.

I would like to present him at this time, David Pickett from Wright-Patterson Air Force Base, will discuss electrochemical methods and electrode fabrication at the Air Force Air Propulsion Lab.

PICKETT: Over the past few years there has been a considerable interest at the Air Force Aero Propulsion Lab in electrochemical methods of impregnating sintered nickel plaques.

Last year I presented some data on experimental cells which had positive plates that were impregnated using the Bell high temperature process. Since this time General Electric has developed, under contract with us, a constant potential process of methodic deposition.

We have developed other methods in-house which are very similar to the Bell process as a result of our experimentation with this process.

This presentation will be concerned with the results of these developments in the form of capacity measurements, loading data and cycle life test data generated on these cells and their plates, but first let me explain the processes to you.

(Slide 52.)

On the first slide I have the recipe for the positive impregnation. In this case we use an ethanol solution. We heat this to boiling and boiling point is about 80° Centigrade, and it is a 1.8 molar in nickel nitrate and .2 molar in cobalt nitrate. We immerse the plaque and make it cathodic and you use either 200 or 270 nickel anodes. Current is then passed at .35 to .5 amperes per square inch of plaque. The plaque is then rinsed several times in deionized water and then dried in a vacuum oven at about 35° Centigrade.

The last step is optional. You can cycle your plaques in the cell if you want to and omit this step.

(Slide 53.)

On the next slide I have a comparison with anodic reactions that occur, and I am comparing these with anodic reactions that occur in the Bell process, so that you can get some idea what is going on.

I believe these electrode reactions that I have here have by no means been proven. These are just possibilities in the case of the ethanol.

Of course, in the cathodic process what happens is that you reduce the nitrate to nitrite or other oxidation states of nitrogen and in the process you remove hydrogen ions from inside the plaque, and this precipitates the active material.

We can also use the ethanol process for cadmium impregnation, but we do not get as good results, or we haven't yet, as we do with the positive impregnation.

In the anodic reaction, in our process, are that the nickel and the cadmium go to the anodes are oxidized to the ion and in the alcohol you get aldehydes and acetic acid in CO_2 form. CO_2 can be in the form of a carbonate, too.

The bulk reaction you get esters. This is evidenced from the smell of the solution. It smells very fruity. Comparing this with the Bell process you get the hydrogen which is generated at the anode, is consumed by the nitrite in the bulk solution.

The negative process that we use is simply to heat an aqueous solution to boiling and make it two molar in cadmium and nitrite and use cadmium anodes and cathodize at 1.6 amps per square inch.

We can load a plaque in about ten minutes to a loading of somewhere between 1.8 to 1.9 grams per cc of void. We would like to do better than this and we still haven't fully developed to our satisfaction.

First let me show you some of the loadings that we do get with the positive plate, though.

(Slide 54.)

This is from loading obtained on a beaker production basis. You can see we get about 1.95 to 1.89 to 2.21 grams of active material per cc of void in the loading. There is a slight increase in the thickness, as you can see, this is from 1 to 2 mils.

(Slide 55.)

AFAPL POSITIVE PLATE IMPREGNATION PROCEDURE

1. Heat 50% ethanol solution, that has been made 1.8 molar in Nickel Nitrate and 0.2 molar in Cobalt Nitrate, to 80-85°C.

2. Immerse nickel plaque (85+ 2% porous) and make cathodic using 200 or 270 Nickel Anodes

3. Pass current at 0.35 to 0.50 amperes per square inch of electrode for one to two hours.

4. Rinse plaque several times in DI water.

5. Dry at 35°C in vacuum oven for ·· or more hours then weigh.

6. (Optional) Cycle plaque at One hour rate charge - one hour discharge discharge for 20 or more cycles.

FIGURE 52

LOADING CHARACTERISTICS OF NICKEL HYDROXIDE ELECTRODES IMPREGNATED FROM ETHANOL SOLUTIONS

(3" x 3" plaques coined 0.010" x 0.100" on all edges)

Plaque #	Wt. After Impreg. (grams)	Wt. of Active Matl. (gms)	Thickness Before (in)	Thickness After (in)	Wt. of Active Matl. per cc of void
1	12.535	5.701	0.0220	0.0239	2.21
2	16.052	6.808	0.0306	0.0372	1.89
3	16.312	7.148	0.0309	0.0321	1.97
4	16.114	7.031	0.0308	0.0319	1.95
5	16.159	6.828	0.0296	0.0307	1.97
6	16.116	6.827	0.0305	0.0320	1.99

FIGURE 54

ANODIC REACTIONS

Inert Anodes

$$2H_2O = O_2 + 4H^+ + 4e^-$$

$$H_2O + NO_2^- = NO_3^- + 3H^+ + 3e^-$$
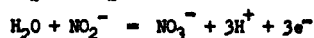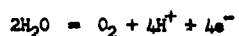
Using Nickel or Cadmium Anodes

$$Ni = Ni^{++} + 2e^-$$

$$Cd = Cd^{++} + 2e^-$$

In Ethanol

$$C_2H_5OH = CH_3CHO + 2H^+ + 2e^-$$

$$C_2H_5OH + H_2O = CH_3COOH + 4H^+ + 2e^-$$

$$C_2H_5OH + 3H_2O = 2CO_2 + 8H^+ + 8e^-$$

BULK REACTIONS

$$NO_2^- + H^+ = HNO_2 \quad \text{(Bell Process)}$$

$$C_2H_5OH + CH_3COOH = C_2H_5OOCCH_3 + H_2O \quad \text{(In Ethanol)}$$

FIGURE 53

PERFORMANCE OF NICKEL HYDROXIDE ELECTRODES IMPREGNATED FROM ETHANOL SOLUTIONS

Plaque #	Theo Capacity [*]	Measured Capacity [#]	% Utilization of Active Matl [&]	A-h per cc of Void	A-h per in [3]	Thickness (20 cycles)
1	1.648	1.399	84.9	8.90	7.28	0.0261
2	1.968	2.208	112.2	10.10	>8.19	0.0370
3	2.066	2.020	97.8	9.14	7.42	0.0347
4	2.032	2.020	99.4	9.17	7.44	0.0344
5	1.973	2.020	102.4	9.55	7.75	0.0328
6	1.973	2.020	102.4	9.64	7.81	0.0330

[*]-- Assuming weight gain due to Ni(OH)$_2$ + Co(OH)$_2$ and Co(OH)$_2$ is active material

[#]-- 2.5 amp charge to 120% of theo. capacity then discharge at 2.5 amps to 0.9 volts. Average of cell with 3,4,5 and 6 taken.

[&]--After 20 charge/discharge cycles

FIGURE 55

On the next slide I have a summary of some of the performance characteristics of the positive plates. These were taken from positive limited cells. These are either 3 or 5 plate cells. First two came from a 3-plate cell and the last 4 plates were from another cell.

You can see the ampere hours per cc of void is roughly about 9 to 10 and the ampere hours per cubic inch measured after 20 cycles is between 7 and 8.

The percent utilization runs as high as 112 percent. This is based simply on the loading and considering both nickel and coablt hydroxide to be active material.

Conditions at which these data were taken are shown. These were given 20 charge-discharge cycles at 2.5 amp charge to 120 percent of theoretical capacity, then discharged at 2.5 amps.

We have actually done better than this on scale-up and this data is shown on the next slide.

(Slide 56.)

We have scaled the process up to impregnation of four 9-1/2 by 8-1/4 30 mill plaques. These are all connected in parallel and nickel anodes are used in a large impregnation tank.

The impregnation tank is polypropylene and is heated by circulating the impregnate solution through a resistance heater, then back into the tank, and then is brought to the boiling point with immersion heaters.

Once you turn on the immerse electrodes and turn on the current, the temperature is maintained.

As you can see in our first impregnation we obtained a loading of about 7 ampere hours per cubic inch theoretical. These plates were taken and made into cells which occupied a volume of about the same as a 22 ampere hour aircraft cell, and I have cycle life data which I will show on those.

(Slide 57.)

As you can see from the last data that I had there I got on the fourth loading that we had we got as high as 9 ampere hours per cubic inch theoretical loading.

This is some capacity data versus cycle life of the negative plates that we make.

The A and B here are plates taken from aircraft cells having the same volume as our electrode.

You can readily detect that the fading in capacity with the other electrodes, whereas the electrochemically impregnated electrode stays fairly constant, and this is in support of what Dr. Holleck said in his presentation.

(Slide 58.)

What I have here is capacity data, a charge efficiency versus state of charge for 22 ampere hour aircraft cells.

This data was taken by Dr. Lander about two years ago for aircraft cells right out of Air Force stock and it was made in order to determine the optimum charging for cells without going into overcharge.

We have run similar data for our cells and these are shown on the next vugraph. You will notice that the lines are very straight in comparison with the aircraft cells and comparison of both these data is given on the next slide.

(Slide 59.)

You can see that we do get an improved charging efficiency with the cells made from this process at the higher temperatures. This is a constant problem in Air Force applications, getting the charging to an aircraft battery at high temperatures experienced in places such as Texas and Arizona during the summertime.

These cells we cycled after we established this data. We cycled them at 110° Fahrenheit to failures. We observed 750 cycles at 100 percent depth of discharge before failure and one cell failed by the active material coming out of the positive plate and shorting the cell.

One layer of Pellon separator was used here.

In comparison your aircraft cells will experience somewhere between 500 and 650 cycles under these conditions.

That is, essentially, what I have to present.

I have a picture showing the impregnation process

SCALE-UP LOADING CHARACTERISTICS OF NICKEL HYDROXIDE
ELECTRODES IMPREGNATED FROM ETHANOL SOLUTIONS

(9. 50" x 8. 25" x 0. 030" plaques including six 2. 75" x 4. 75" electrode areas
with .20" coining between areas, 0. 100 around edges)

Plaque #	Wt. of Active Matl.	Wt. of Matl. per cc void*	Theo. Capacity	Thickness gain on Impreg (in)	Theo. Ah/in³
SU-1	58. 80	1. 73	16. 99	. 0016	7. 0
-2	57. 60	1. 70	16. 64	. 0028	6. 7
-3	58. 40	1. 72	16. 88	. 0031	6. 8
-4	59. 00	1. 74	17. 05	. 0026	6. 9
-13	77. 50	2. 29	22. 40	. 0036	9. 0
-14	75. 85	2. 24	21. 92	. 0025	8. 8
-15	77. 60	2. 29	22. 47	. 0036	9. 0
-16	78. 45	2. 31	22. 67	. 0040	9. 3

FIGURE 56

CHARGE EFFICIENCY VS STATE OF CHARGE
AIRCRAFT CELLS

FIGURE 58

COMPARISON OF
CAPACITY VS CYCLE NO.
FOR COMMERCIAL & AFAPL
CADMIUM ELECTRODES

FIGURE 57

CHARGE EFFICIENCY VS STATE OF CHARGE
AIRCRAFT CELLS _____
AFAPL CELLS ....

FIGURE 59

110A
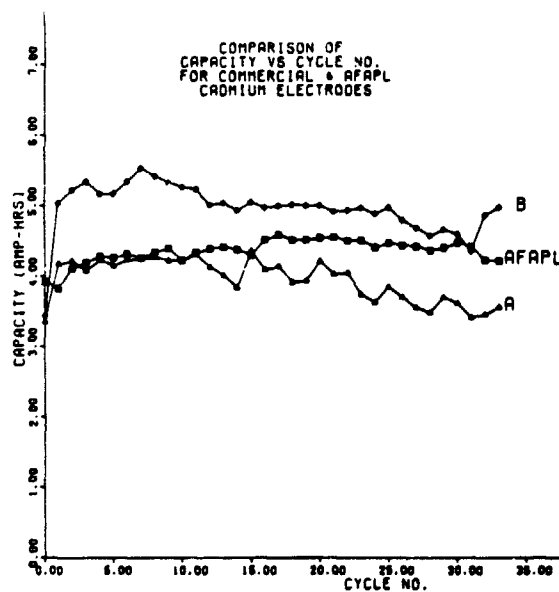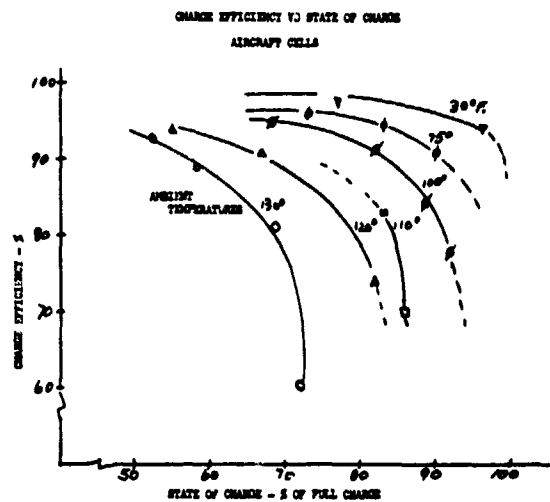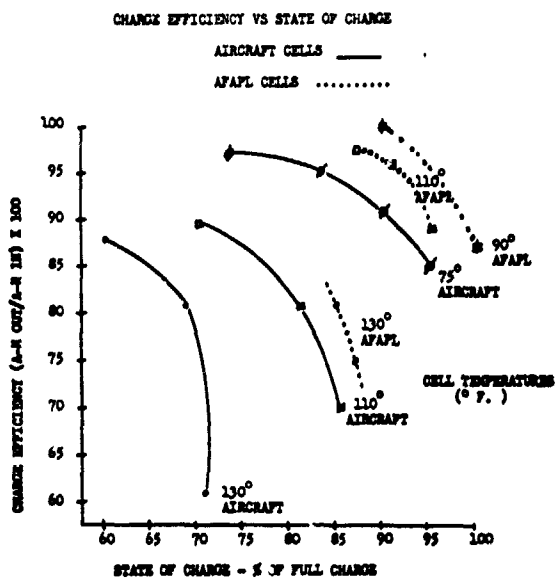
with scale-up.

          These are the plaques here that he is putting
in a tank, and these are the nickel anodes used. Then
the solution is heated by circulating it through this
heater here.

          HALPERT: Are there any questions for David
about this process?

          PARK: The only question was, on the 35,000 cycle
what was the depth of discharge?

          PICKETT: There was 750 cycles, sir, and those
were one hundred percent depth of discharge.

          PARK: Pardon me, but I thought I saw one curve on
the abscissa that looked like 35,000 to me.

          PICKETT: No, that was ampere hour capacity.

          PARRY: How long do the nickel anodes last?

          PICKETT: Depends on what you use for the anodes.
If you use 200 nickel it will go quite readily. If you use
280 they will last quite a long time.

          PARRY: Do you anticipate this would be a problem
in scale-up or general practice of this procedure?

          PICKETT: It could be a boon if you can put your
nickel back in the solution with anodes.

          GASTON: What charge regime did you use in getting
the 750 cycles?

          PICKETT: Constant potential charge at 1.7 volts.
Discharge at about one hour rate.

          BELOVE: When you were comparing cells, one of
the cells you tested had one layer of Pellon?

          PICKETT: Both had one layer of Pellon for
separator.

          BELOVE: When you mentioned standard aircraft
batteries generally used two or three layers of separator --

re42

PICKETT: That is right.

BELOVE: -- so that when you were comparing the two weren't you comparing batteries with three layers to batteries of one layer?

PICKETT: To some extent, yes.

BELOVE: If you were using one layer of Pellon, would you expect to be able to do constant potential charging for long periods of time without running into thermal runaway?

PICKETT: Well, we control the charge voltage very well on these and watch them very carefully.

BELOVE: Yes, I know, unlike the uncontrolled voltage onboard aircraft.

PICKETT: Right.

Let me add one more thing to Mr. Belove's comment. We are trying to cycle these under conditions that aircraft cell experiences.

BELOVE: I missed that.

PICKETT: We were trying to charge these the way aircraft cells are charged, is the reason we use the constant potential charge.

BELOVE: Yes, I agree there. But you see where I disagree is this: you were using 1.7 volts, which is generally much higher than what is used onboard aircraft.

PICKETT: Yes, that is right.

BELOVE: It is a worse condition, I will grant you that, and that is why I mentioned the fact that if you had gone on to overcharging you would have run into a great deal of difficulty.

PICKETT: Right.

KLEIN: What type of nickel plaque were you using there, anything special?

PICKETT: No, there is nothing special about the

plaque, I will assure you of that. It is standard pro-
duction plaque made by Eagle-Picher. I don't think there
is anything special about it, is there, Earl?

(Laughter.)

PICKETT: Eighty-five percent porosity plaque.

HALPERT: Anyone else?

MAURER: What pH do you have in a vat?

PICKETT: Well, in an ethanol solution -- now,
this becomes a complex problem because you can no longer use
pH as a scale for acidity. We have measured the pH, but
what you get in number you have a hell-a-va pH meter, it is
not actually pH. It is just a number. On a pH scale this
roughly is somewhere between 2 and 3 to start with, and at
the end it is about 5.

The negative impregnation, we don't bother to pH
it at all.

HALPERT: Anyone else?

(No response.)

HALPERT: Thank you, David.

(Applause.)

HALPERT: Our next speaker this afternoon has
done a great bit of work with process variables in the plaque
work and impregnation work at Eagle-Picher. Lee Miller will
summarize the process variable study program.

MILLER: I was just recently informed that I had
15 minutes to make this paper in and it really should have
taken me about 45 minutes, so I will have to move right along.

The purpose of my paper today is to briefly sum-
marize a two year program which we have titled a "Study of
Process Variables Associated With Manufacturing Hermetically-
Sealed Nickel-Cadmium Cells." The program resulted from
NASA/GSFC Contract No. NAS5-21159 Mr. Floyd Ford served as
the technical monitor, and I would like to take this oppor-
tunity to express our appreciation for his guidance and
suggestions relating not only to program direction, but also
to interpretation and presentation of results in the published
reports.

The overall objective of the program was to develop process procedures and controls for manufacturing nickel-cadmium aerospace type cells with reliable five year life capabilities.

The philosophy of our approach to meet the stated objective assumed our present manufacturing state-of-the-art was capable of producing cells which would meet five year life requirements. However, to do so reliably would require significant improvement in product uniformity. With an emphasis then on defining and controlling process variables which have a significant effect upon manufacturing, the scope of work for the program was divided into the following four phases.

Phase I consisted of a detailed analysis of our manufacturing procedures in conjunction with a review of the available pertinent literature concerning nickel-cadmium cell manufacturing. The objective of this phase was to assess the critical process variables associated with the manufacturing process.

Phase II involved the design and performance of experiments to verify and measure effects of the process variables selected for investigation in Phase I and possibly identify and measure additional process variables.

Phase III consisted of the preparation of manufacturing, procurement, and quality control specifications reflecting the controls and improvements suggested in the previous phases.

The final phase, Phase IV, which is not yet complete, will involve the implementation and "prove out" of Phases I through III. Cells will be fabricated, tested and delivered, incorporating the advances in the manufacturing state-of-the-art evolved from the total program.

As a result of the size and length of this program, this paper will be primarily concerned only with Phase II, or the actual experimental work performed.

(Slide 60.)

We used a new statistical technique in this program which we call a regression analysis. It offers advantages that in many of these experiments you have a great deal, or a large number of variables effecting a particular response, like impregnation, pick-up weight, maybe a function of solution,

specific gravity, heat, time impregnation, whether it is in a vacuum, and so forth.

The results of the regression presents what we call a regression equation, and through the interpretation of the coefficients, in this case b, c, d through N, the regression determines the effect upon the X variables on the Y of interest.

The first area of study we call the sintered plaque process study, and this photograph just simply presents our facilities. At the left you have a plaque forming area. In the middle there the incendiary furnace and the cooling zones. In the background is the atmospheric generation or the reducing atmospheric generation equipment.

(Slide 61.)

We also use the fractional factorial designs that have been mentioned previously, to determine what variables and what levels of variables would be investigated, and in this case we chose two levels.

You see here there are seven variables in the sintered plaque process and they were all regressed against two responses shown below with plaque strength and plaque void.

(Slide 62.)

This is our four point bin tester for making the plaque mechanical stream evaluations. The sample is placed into the area in the upper portion of the photograph and the arm there moves down and applies pressure to the load cell and it is recorded on this chart on the lower left-hand corner of the photograph.

(Slide 63.)

This summarizes the results of the regression analysis on the sintered plaque process study.

I am just including these in here so that at the end of the proceedings anyone who has some special interest in them can then go over them leisurely.

REGRESSION ANALYSIS, BASIC PRINCIPLES

PROBLEM

$$Y \text{ vs. } X_1 \quad X_2 \quad X_3 \ldots Xn$$

REGRESSION ANALYSIS

TWO VARIABLES
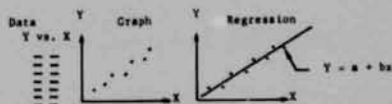
THREE VARIABLES
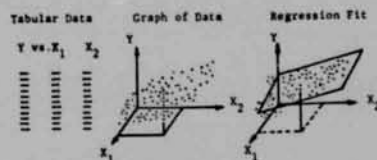
REGRESSION EQUATION

$$Y = a + b (X_1) + c (X_2) + d (X_3) + \ldots + N (Xn)$$

Interpretation

Evaluation of coefficients b, c, d, ..., N reveal main effects.

Prediction

Substitution of different variable values permit prediction for Y under levels and combinations of levels not tested.

FIGURE 60

FIGURE 62

SINTERED PLAQUE PROCESS STUDY

FACTORIAL VARIABLES & DESIGNATION OF LEVELS

VARIABLES (X Values)	LEVEL AND DESIGNATION
1. Temperature	1600 - 1850 Degrees F
2. Belt Speed	6 - 12 Inches/Minute
3. Dewpoint	25 - 50 Degrees F
4. Atmosphere Amount	400 - 800 Cubic Feet/Hour
5. Bulk Density	Measured, .870 ± .006 gms/cc
6. Plaque Spacing	0 -16 Inches
7. Cooling Zone	75 - 175 Degrees F

RESPONSES (Y Values)

1. Plaque Strength

2. Plaque Void

FIGURE 61

SINTERED PLAQUE PROCESS STUDY
REGRESSION ANALYSIS RESULTS

(1) Dewpoint exhibited greatest effect. Lower dewpoint, higher strength and lower void. Incorporate increased control.

(2) The next greatest effect was exhibited by sintering temperature. Higher temperature, greater strength and lower void. Incorporate increased control.

(3) Reducing atmosphere volume exhibited effect next in magnitude. Higher volume, increased strength and decreased void. Incorporate increased control.

(4) Slow belt speed produced plaques with high strength and low void. High speed, just the opposite.

(5) Cooling zone temperatures exhibited little effect upon strength and void.

(6) Strength and void appear to be inverse linear functions.

FIGURE 63

(Slide 64.)

Besides indicating a number of areas that
required additional control on our sintered plaque process,
we also in regression identified that there was significant
variability within any particular plaque. We felt that
this was introduced to our hand forming operation in which
an operator just actually form the dry sintered powder plaque
before it was sintered.

This system here was referred to as a semi-
automatic plaque forming too soon. It was a subject of a
paper last year by Mr. Bob Howard.

What it does is take all the variability that is
introduced by the hand operation system.

You have up above our drain device which meters
a specific amount of the dry powder and then your arm which
actually forms the plaque, which moves down on these rails,
are controller under extremely mechanical tolerances to give
you a uniform plaque each time.

(Slide 65.)

The next area of study referred to is the
impregnation/polarization and formation in our research and
development area. This shows in the lower left-hand corner
the reservoir tanks, the smaller of the two large tanks
there is the impregnation/polarization, and the larger tanks
the formation. Also the ionized water column system. In
the background we have the power systems for polarization
and formation.

(Slide 66.)

This is the fractional factorial design experi-
ment for the impregnation/polarization process study. In
this case we looked at 21 variables and the results were
regressed against this lower variable, this number 21. There
were three plaques selected from the previous sinter plaque
process study. Using the information gained from the regress-
ion we fabricated three groups of plaques.

One, was the low void high strength, medium void
medium strength, and high strength low void. Had these para-
meters and were placed into the impregnation/polarization
experiment to determine the effect of the plaque character-
istics.

Responses are impregnated pick-up weight, electrical capacity and plaque characterization.

Characterization is really a subjective estimate of evaluation of the plaque's physical appearance. If it was smooth, no cracks, uniform appearance, we gave this a high rating and a low rating for just the opposite.

(Slide 67.)

Here are the results, the regression results for this phase of the program. Again, I will just let you read those yourself, and the data will be available in the proceedings of this conference.

(Slide 68.)

The last area of study which we used regression analysis fractional factorial design experiment technique on was the formation process. In our manufacturing process we have a step which we refer to as formation, in which we actually overcharge the plaques and potassium hydroxide against electrodes to effect electrochemical cleaning process.

Again, you see the three variables of interest in the levels selected and the responses are the same as in the preceding experiment, except we are now interested in the final pick-up weight.

(Slide 69.)

This is the result of formation experiment and, again, I will let you read those and they will be available in the proceedings.

(Slide 70.)

Associated with the formation process is the final plaque washing operation. At this point we designed the residual caustic plaque removed in order to prevent the subsequent carbonate formation.

Usually to evaluate whether the plaques are adequately washed, the plaque is periodically removed from the process and by the last drip method the runoff, the pH of the runoff, is measured. If it is approximately neutral or acidic we assume that the washing is adequate. However, in the past we have always used pH paper for this test and we experienced considerable durations in the length of time

FIGURE 64
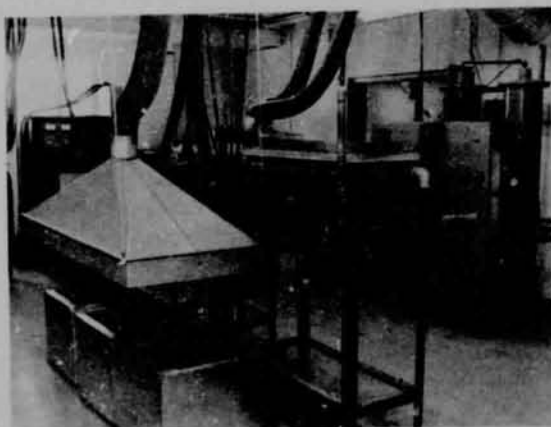
FIGURE 65

IMPREGNATION/POLARIZATION PROCESS STUDY

FACTORIAL VARIABLES (X Values)	DESIGNATION	LEVELS NEGATIVE	POSITIVE
1	Specific Gravity of Nitrate	1.800-1.900	1.700-1.800
2	Free Acid	.2-.5 gm/liter	1-4 gm/liter
3	Temperature of Nitrate	110°F-140°F	140°F-200°F
4	Time of Impregnation		15 Minutes - 1 Hour
5	Vacuum		0-15 Inches
6	Wash Time		10-30 Minutes
7	Wash (Number of Cycles)		1-3
8	Wash Water Temperature		R.T. - 150°F
9	pH of Wash Water		Measured
10	Type of Caustic		KOH-NaOH
11	Specific Gravity of Caustic		1.200-1.300
12	Temperature of Caustic		80°F-150°F
13	Amount of NH_3 in Caustic		Measured
14	Amount of CO_2 In Caustic		Measured
15	Amount of OH in Caustic		Measured
16	Polarization Current		.1-.4 Amps/sq. in.
17	Polarization Time		15 Minutes-1 Hr.
18	Voltage of Plaque to Ref. Electrode		Measured
19	Amount of Cycles with Same Caustic		1-5
20	Number of Total Cycles		Measured
21	Type of Plaque		3 Types

RESPONSES (Y Values)

1 Impregnated Pick-up Weight
2 Electrical Capacity
3 Plaque Characterization

FIGURE 66

IMPREGNATION/POLARIZATION PROCESS STUDY

REGRESSION ANALYSIS RESULTS

Preference indication in optimization process:

VARIABLES

1   High specific gravity preferred in positive process, low preferred in negative process.

2   Low free acid preferred in positive process.

3   High nitrate temperature preferred.

4   Longer impregnation time preferred.

5   0 vacuum preferred.

10   NaOH preferred caustic.

11   High NaOH specific gravity preferred.

12   High NaOH temperature preferred in positive process, low temperature preferred in negative process.

16   High polarization current preferred.

17   Short polarization time preferred in positive process, longer times preferred in negative process.

21   High strength, low void plaques preferred in positive process, low strength, high void plaques preferred in negative process.

FIGURE 67

required like four hours one time and twelve hours the next time, using pH paper.

We chose another indicator which was the liquid phenol phthalein indicator. This graph presents partially what we measured at this point. This is a quantitative measure in the residual caustic.

At approximately the four hour period on this test, using pH paper, we measured acidic level just slightly past the four hour period. Using the phenol phthalein indicator we could not measure an acidic or a neutral level for approximately 24 hours.

I think the conclusions of this are the phenol phthalein are a much more sensitive indicator for this test and should be used in place of pH paper.

(Slide 71.)

We also studied carbonate contamination during the program, and I think we have drawn basically the same conclusions that have already been presented here, in that, the major carbonate contamination source, at least on the initial phases, are from the plates themselves. We tried several experiments to reduce this level without too much success, and up to this point always assumed that the carbonate was really the conversion of the residual caustic in the polarization/formation experiments, but we had the plates most specifically analyzed for potassium and sodium ion and found that the level of both of these ions was much too low to justify the assumption that residual caustic was a source of carbonate.

I, then, my personal opinion, assume that is possible that the acting material in hydroxides in the plaques do, to a certain extent, convert to carbonate in their exposure to the atmosphere.

We have found that by handling the plaques very carefully, like maintaining them under water during the impregnation/polarization process between steps, sealing them in polyethylene, and by experience in shipment and storage and awaiting fabrication and then during fabrication again resealing the cells, the plates and electrodes that we could control and maintain carbonate levels, measured down in the order of one to two percent plate weight. This device here was an electrolyte activation technique that was developed, associated with this attempt to reduce carbonate.

FORMATION PROCESS STUDY

FACTORIAL VARIABLES

(X Values)

	LEVEL	
	0	1
1. Percent Charge	110	200
2. Specific Gravity	1.20	1.40
3. Formation Time (Hours)	4	24

RESPONSES

(Y Values)

1. Final Pick-up Weight
2. Electrical Capacity
3. Plaque Characterization

FIGURE 68

FIGURE 70

FORMATION PROCESS STUDY
REGRESSION ANALYSIS RESULTS

1. High percent charge introduced over short period of time is preferred with respect to electrical capacity in the positive process; however, the effect upon final pick-up weight and plaque characterization limits this procedure and requires strict control.

2. Low percent charge introduced over a longer period of time is preferred with respect to electrical capacity in the negative process; in this case, plaque characterization or electro-chemical cleaning effect is the limiting factor.

3. No significant effect could be attributed to specific gravity of caustic.

FIGURE 69
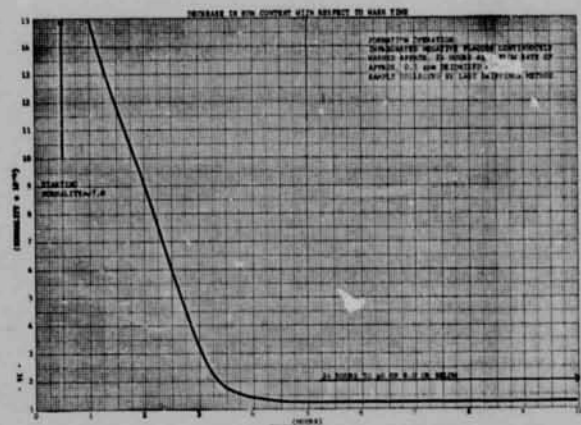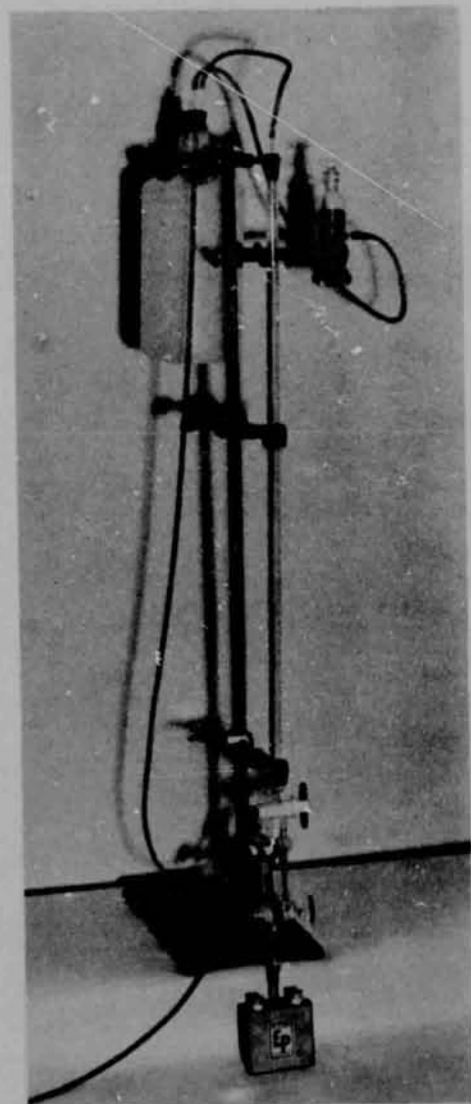
FIGURE 71

(Slide 72.)

This drawing shows it a little bit better, I believe.

This refers to the vacuum burette activation technique and it offers advantages, in that, it is closed to the atmosphere as far as CO_2. These bulbs that you see up here in the right-hand corner are CO_2 absorption bulbs. The system is rather fast. I can activate a cell in 60 to 90 seconds within an accuracy of a half of one percent.

(Slide 73.)

The last phase which I am going to discuss today refers to the parametric cell study. In this group we attempted to look at a number of selected process variables on the actual cell level.

Going down the list we employed, we suggested a lower electrode loading in cells in the levels indicated. They received what we call three formation cycles.

Really, these are 24 20 ampere hour cells divided into four parametric cell groups.

The second level is moderate electrode loading at the levels indicated, containing only one formation cycle.

Backup just a second.

The major variables that we looked at in this phase of study were light loading versus heavy loading, low formation cycle versus numerous formation cycles. We also looked at vacuum drain of plaques. We thought that this might be a technique for reducing the carbonate in the plates. We looked at reversed plates during formation, in other words, instead of just overcharging we drove the plates into reversal to revolve the adds from the other direction to effect even superior clean or the possibility thereof.

Getting back to it, group 3 was moderate electrode loading 10 formation cycles.

Group 4, moderate electrode loading, and in this case the plaques were vacuum dried during the processing.

Group 5, heavy electrode loading levels indicated, three formation cycles.

The final group of moderate electrode loading, plaques discharged during formation.

(Slide 74.)

The main purpose of these cells really is the life cycle test at Crane, and they are on their way there at the moment, but we did run some preliminary characterization tests, and this summarizes these tests at various temperatures.

During the first 75° test, making some general observations, the first point that was observed is that group 5 or group 4, the vacuum dry flax pressured rapidly. As a matter of fact, I think they had to be taken off charge, because they reached a level, or we decided to let them go to 100 psi.

Another item on there is that the heavily loaded plaques, group 5, did not give us any more capacity than the moderately loaded plaques.

In the 32° test it became obvious that the lightly loaded plaques, group o, and the additional formation groups, group 3, had superior or lower voltage, charged voltage characteristics, than the other subgroups.

We did some some higher pressures on the group 2 and group 4 furnace test. In the 95° test, generally the cells demonstrated higher pressures, except for possibly group 3 on the additional formation cycles, but in this particular group the charge efficiency appeared to be quite low relative to the others.

In the last 75° test the results were fairly similar to the first 75° tests, however, in this case the flax , which were vacuum dried during processing and the recombination characteristics, have improved significantly.

(Slide 75.)

In this last slide we looked at the charge efficiency versus several parameters. In the first group, our first comparison, looked at the 75° capacity versus theoretical. As you can see, group 1 light loaded is somewhat inefficient. Groups 2 is very good, one formation cycle.

Group 3, additional formation cycle is very poor.

VACUUM BURETTE INDIVIDUAL
CELL ELECTROLYTE ACTIVATION
SYSTEM
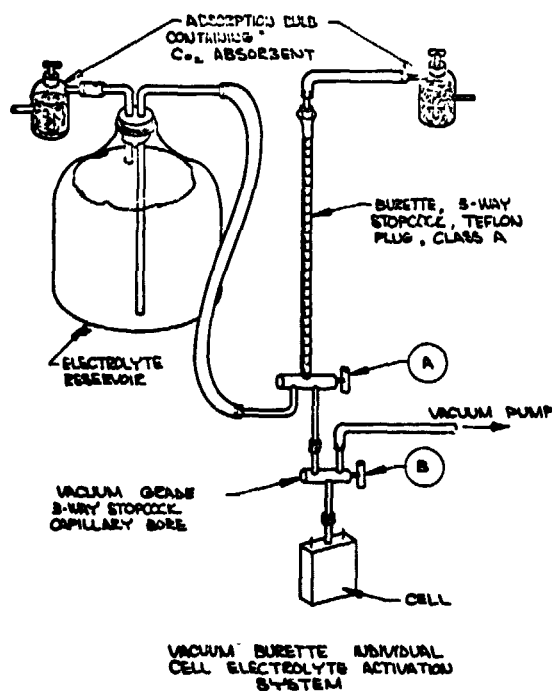
FIGURE 72

PARAMETRIC CELL PERFORMANCE DATA

GROUP	I	II	III	IV	V	VI
TEST TEMPERATURE 75°F						
PV	1.425	1.433	1.420	1.442	1.432	1.423
PP	10	30	10	100	35	55
AH	17.7	27.0	24.2	26.5	26.4	22.5
TEST TEMPERATURE 32°F						
PV	1.486	1.515	1.465	1.520	1.520	1.514
PP	30	80	9	90	55	55
AH	16.3	25.4	22.5	25.0	25.0	21.3
TEST TEMPERATURE 95°F						
PV	1.398	1.400	1.380	1.397	1.404	1.83
PP	85	100	55	100	60	70
AH	11.3	21.7	12.5	20.5	23.3	20.0
TEST TEMPERATURE 75°F						
PV	1.455	1.468	1.425	1.460	1.470	1.475
PP	35	55	·3	40	25	80
AH	17.5	27.2	22.8	27.0	27.3	22.8

FIGURE 74

PARAMETRIC CELL PARAMETER LEVELS

CELL SIZE 20 AMPERE HOUR, SAMPLE SIZE 24 CELLS, 4 CELLS/PARAMETER.

GROUP   I   LOW ELECTRODE LOADING, 0.5-0.6 GRMS./SQ. IN. POS.;
0.7-0.8 GRMS./SQ. IN. NEG.; THREE (3) FORMATION CYCLES.

II   MODERATE ELECTRODE LOADING, 0.7-0.8 GRMS./SQ IN. POS.;
0.9-1.0 GRMS./SQ. IN NEG.; ONE (1) FORMATION CYCLES.

III   MODERATE ELECTRODE LOADING, TEN (10) FORMATION CYCLES.

IV   MODERATE ELECTRODE LOADING. PLAQUES VACUUM DRIED
DURING PROCESSING, THREE (3) FORMATION CYCLES.

V   HEAVY ELECTRODE LOADING, 0.9-1.0 GRMS./SQ. IN. POS.;
1.1-1.2 GRMS./SQ. IN NEG.; THREE (3) FORMATION CYCLES.

VI   MODERATE ELECTRODE LOADING, PLAQUES OVER DISCHARGED
DURING FORMATION, THREE (3) FORMATION CYCLES.

PARAMETRIC CELL CHARGE EFFICIENCY DATA

GROUP	I	II	III	IV	V	VI
75°F CAPACITY VERSES THEORECTICAL						
%	72	92	78	91	70	80
32°F CAPACITY VERSES 75°F CAPACITY						
%	92	94	93	94	94	95
95°F CAPACITY VERSES 75°F CAPACITY						
%	64	80	52	77	88	89

FIGURE 75

FIGURE 73

120A

Group 4, the vacuum dry flax is very high. efficiency.

Group 5 the heavily loaded plaques has poor efficiency.

Group 6, reversal and moderate efficiency.

In the 32° capacity versus 75° capacity test, all the cells seem to have a fairly good efficiency relative to the 75° capacity.

In the final capacity of utilization measurement in the 95° test, the group 3, the cells which received the additional formation cycles, really stand out, in that, they have very poor efficiency. This is somewhat hard to understand.

The next level of poor efficiency in the 95° test is group 1, the lightly loaded plaques.

Again, the evaluation of these cells is not complete. They are destined for a life cycle test at Crane.

This completes a very hurried presentation of my original paper.

HALPERT: Any questions of Lee about his study?

MILLER: Looks like I danced right around them.

HALPERT: Thank you, Lee.

(Applause.)

HALPERT: Our next speaker of the afternoon has done some work in our lab under the direction of Federal City College with Federal City College. Clinton Jones has been doing some work with the negative electrode and looking at the effects of washing the negative plate with charged active material in it. We know that there is obviously an effect of oxygen recombining with the negative, but the question is, to what extent, and he has done some work to show that.

I will present Clenton Jones, Federal City College.

JONES: The work that we have been doing in this particular area was taking some plates and charging

them and discharging them under different conditions.

(Slide 76.)

Now, we ran four different tests that you can see here.

To begin with the plates were formed and that charged at a .3 amp hour rate for a period of 1.2 hours. Now, the total input of those particular plates were 3.87, as you can see in the corner here.

The plates were divided into two sections. One section was washed in deionized water; dried in a vacuum oven or open atmosphere type. They were washed for a period of one hour, they were dried overnight.

The remaining half stayed in, what they were charged in.

After drying overnight the plates were taken, put back into the cell and continued to discharge.

We found that the ones that were washed, the total output was 2.37. The ones that remained in the cell and were never removed were 3.42, which shows that there is some loss in capacity due to that particular condition.

The second test we ran were the same procedures again. They were charged for 1.2 hours, divided into two sections, and again they were washed in deionized water. This particular time it was in a controlled atmosphere chamber where the deionized water was practically O_2 free, we bubbled nitrogen through it for a period of a half hour prior to putting the plates in it. This was done for a period of one hour.

Again, the plates were taken out of the wash, dried inside the chamber overnight. The following morning they were taken out, put back in the cell and again discharged.

Here we see the difference of 3.8, 3.48 for the cells that were washed under these conditions, and 3.69 for the ones that remained within the cell.

SAFT AEROSPACE ELCTRODES NEGATIVES N° 1694-845-557

INPUT	CONDITION	OUTPUT	
		WASHED	NOT-WASHED
(-3 AMPS-CHG. RATE) 3.87	DEI. WATER AIR-ATMOSPHERE 1 HR.	2.37	3.42
3.85	DEI. WATER – O_2 FREE NITROGEN ATM. 1 HR.	3.48	3.69
3.87	DEI. WATER – C.F. NITROGEN ATM. ½ HR.	2.35	3.50
7.50 3.75	DEI. WATER – C.F. NITROGEN ATM. ½ HR.	2.28	3.32

FIGURE 76

122A

The third test, again it was the same, charged
for 1.2 hours. Again they were washed in deionized water
in a controlled atmosphere chamber, but this particular
time we tried to create a situation where they were washed,
with a continuous flow of
deionized water, where the water is flowing constantly over
the plate. To check to see if they were sufficiently washed
or if all the electrotyle were washed out, we used phenol
phthalein as an indicator and we would take the plates and
with a drop of the water off them, if there was no color then
we assumed that all of the electrolyte had been removed by
the washer. This took a period of about half an hour for
this to occur.

After, when the plates were in the chamber, they
were allowed to dry overnight and the following morning we
discharged them. As you can see, we have a total input of
3.87. The plates that were washed 2.35 and the ones that
remained in the cell were 3.50.

The last and final test, we wanted to check to
see what, if any, effect discharging the plates prior to wash-
ing them or discharging them partially prior to washing them.
This particular time we charged the plates for 2.4 hours,
a total input of 7.50. We discharged them at the same rate
which was .3. I will leave the charge and discharge at .3
ampere hours down to 3.75.

Then the plates were put in a controlled atmosphere
chamber, washed in deionized water, as before, with a con-
tinuous flow in deionized water. They were tested to see if
they were sufficiently washed by the same method as before
by using the phenol phthalein indicator and dropping it off
the plates, and this took a period of about a half hour.
Again, they were allowed to dry overnight in the chamber
and were discharged the following morning.

So the total input that we had at the particular
time was 3.75. As to the washed ones we took out at 2.28, and
the ones that remained in the cell were 3.32.

Now, from those particular tests we conclude that
the presence of oxygen has a direct role in the amount of out-
put that we received from the plates.

Now, the first condition, I guess, from about 20
to 30 percent of what the original input was.

The second where there was practically O_2 free we get
approximately 90 percent of what was put in.

The third where there was oxygen only within the water, in the deionized water that we used, we got about 30 to 40 percent of the total.

The last one was approximately the same, about from 35 to 40 percent. Of the total input of the amount we put in there was about 40 percent of the ones we washed.

So in general conclusion, I would say that the presence of oxygen in the charging and washing and discharging of those particular plates definitely played a role. The places where there was little oxygen the input was close   to the amount we received out of unwashed   cells.

HALPERT: Thank you, Clenton.

Are there any questions for Clenton?

(No response.)

GASTON: I think the key thing here is not only the fact that oxygen obviously effects the charge negative, but to the extent to which it is effected in a half hour of washing in nitrogen-free water and drying for an overnight period we still retain 90 percent of the charged active material. In the other case almost 70 percent after washing, we still had charged negative material in the plate.

HALPERT: Thank you, Clenton.

(Applause.)

HALPERT: Steve Gaston would like to speak on the subject of electrode weight and thickness from some statistical data, and he also has some discussion about electrolyte filling.

While he is still up here we will have him continue on both subjects.

GASTON: Could I have the first slide, please.

(Slide 77.)

What I have is a short summary of some hundred amp hour electrodes which were made in using the semi-automatic plaque laying process for Eagle-Picher, and I think it was discussed at the last workshop meeting.

re55

If you use that process and the process variable studies input to make the hundred ampere electrodes, the first group of one hundred ampere hour electrodes which came out from the semi-automated plaque laying process, which is designated as development group 3, we have a later group which we haven't analyzed yet, we have two types of electrodes.

We have two types of positives, a thin positive and a baseline positive. The thin positive is approximately 22 mils and the baseline is about 29 miles. The same thing we have two types of negative electroes, a thin and baseline.

We have a sample here about 195 on the thin positive and we weigh every one of them to the nearest tenth of a gram and we determine a mean range and a percent tolerance. We did this for all the electrodes and we get the same thing on the thickness, the caddy guage was used by Eagle-Picher and determined the thickness.

When you compare the two tolerances the thin negatives have a larger tolerance than the baseline negative, because they are so much thinner they are a little more delicate.

When you compare the tolerances the weight tolerances are relatively close to the thickness tolerances, and so there should be a pretty close correlation between both of them. So the densities should be pretty uniform, which is of special interest, since the electrodes, I think I mentioned before, it is about 7 inches by -- actually it is a trapezoid design, one dimension is 6-1/4 and the other one is 6-1/2, it kind of slopes downward, and the average being 5-7/8, and results in about 41.2 square inches. This is a relatively large electrode and we were concerned with the uniform and density of the larger electrode. We also were concerned about the dry process by which they were produced at one time. There was a concern that we might not get uniform density.

What is interesting on the thickness, we apparently can meet the NASA high spec requirements plus or minus one mil, because the negatives we have not been quite that successful. We have plus or minus 2 mils.

I believe an effort was made to keep that tolerance a little bit closer. I think this one will be closer.

The general results I think look good and I think

the semi-automatic process has resulted, although I don't have the data, the electrodes that were made before, but there was a problem of uniform density. I think they are coming along very nicely in this respect.

That is all I have to say on the electro data summary.

Shall I go on to the next one, cr are there any questions on that?

RUBIN: Steve, is that data on completed electrodes or just the plaque?

GASTON: Completed electrodes.

RUBIN: Of that variation in weight, what fraction of that is the sinter and what fraction of that is the active material?

GASTON: I don't know offhand. I would have to think back, maybe I can get that information. Offhand I don't know.

RUBIN: Of that variability in the last column, is that reflected in the capacity variability of the cells or plaques?

GASTON: These electrodes were mixed and they were used in different cells, so I cannot tell. We didn't keep them separate. I cannot tell from the capacity performance which electrodes were which.

Any other questions?

(No response.)

Could I have the next slide.

(Slide 78.)

The next slide reflects, I don't know whether it is a new technique, but it is one technique which we established to get a more uniform electrolyte volume into cells.

This data would sense a number of cells. There are eight development cells. They had thin electrodes, they had baseline electrodes, they had nylon and polypropylene, and some had 17 electrodes, 17 positives and 18 negatives.

All right, this is thin plates. We had the nylon. These are baseline which are standard plates which had polypropylene, the WEX 1242. I should have added all the separator was washed in this case.

We had another group of thin plates, and in this case it is just an isolated sort of an electrode, it shouldn't have any effect on performance, and it doesn't.

These are just group designations to keep them classified as a group. These had 19 positives and 20 negatives. We had 17 positives and 18 negatives all the way through. We went as high as 20 positives and 21 negatives. It is mainly because when you have thinner plates you can add more electrodes.

We did measure the electrolyte volume. We measured the free volume by venting the cell and using nitrogen gas at constant temperature, so this would determine it was measured.

Then the next column shows the combined volume of these two, the electrolyte volume and the free volume. This is a number which was calculated before we went to volumetric filling. We used a percent weight, percent core weight or percent electrolyte to the core weight, which was a previous way of determining how much electrolyte ought to be added to the cell. So this was a previous way of doing it.

What we then had done, we calculated the inside cell volume. We subtracted from the inside cell volume, subtracted the combined electric volume, which is the free volume, and the electrolyte volume and we weighed the core to determine the core weight of each cell, and then we calculated a core volume density. We found we have a relatively uniform core volume density which comes to about 6.13, and the standard abbreviation for relativity, and so based on that for all these designs we calculated an apparent core density and it comes to 6.13 grams per cc.

(Slide 79.)

Based on that, we came up with a number of equations, but provided, we said, the inside volume equals the free volume, plus the electrolyte volume, plus the core volume, or the inside volume. All right, this is just the shorthand.

100 A.H. CELL DEVELOPMENT

DEV. GROUP III ELECTRODE DATA
SUMMARY

A. WEIGHT

ELECTRODE TYPE	NO. OF SAMPLES	WEIGHT IN GRAMS MEAN	RANGE	% TOLERANCE
THIN POSITIVES	195	57.0	55.0-60.0	± 4.4
BASELINE POSITIVES	41	68.8	65.0-72.0	± 5.0
THIN NEGATIVES	203	64.4	59.0-69.0	± 7.8
BASELINE NEGATIVES	40	78.8	75.0-81.0	± 3.8

B. THICKNESS

ELECTRODE TYPE	NO. OF SAMPLES	THICKNESS IN MILS MEAN	RANGE	TOLERANCE MILS	%
THIN POSITIVES	199	21.2	20.3-22.2	± 1.0	4.7
BASELINE POSITIVES	36	26.5	25.9-27.5	± 0.8	3.0
THIN NEGATIVES	204	23.5	21.8-25.0	± 1.6	6.8
BASELINE NEGATIVES	38	31.0	29.0-32.5	± 1.8	5.8

FIGURE 77

Definitions:

Inside Volume (IV) = Free Volume (FV) + Electrolyte Volume (EV) + Core Volume (CV)

1. OR $IV = FV + EV + CV$

   For This 100 AH Cell

   IV = Calculated cell inside volume = 1164 cc
   CW = Core weight in grams
   CV = Core weight in grams divided by 6.13 g/cc

   6.13 = Apparent density of core material. This value was calculated from the development cell free volume and core weight measurements - see attached table.

2. Therefore eq. 1. becomes:

   $$1164 = FV + EV + \frac{CW}{6.13}$$

3. For a free volume goal = 100x %

   $$1164 = FV + (1-x)EV + \frac{CW}{6.13}$$

   $$(1-x)EV = 1164 - FV - \frac{CW}{6.13}$$

   $$EV = \frac{1164 - FV - \frac{CW}{6.13}}{1-x}$$

   $$EV = \frac{1164 - FV - 0.163CW}{1-x}$$

4. For a 50% free volume goal, EV = FV
   Then equation 2. becomes

   $$1164 = 2EV + \frac{CW}{6.13}$$

   $$2EV = 1164 - \frac{CW}{6.13}$$

   $$EV = 582 - \frac{CW}{12.26}$$

FIGURE 79

TABLE 1. 100 A.H. CELL FREE VOLUME DATA

DESIGN DESCRIPTION	CELL S/N	DESIGN GRP. NO.	NO. +/-	ELECTROL. VOLUME cc	FREE VOLUME cc	CORR. ELECTROL. + FREE VOLUME cc	% ELECTROL. VOLUME OF CORR. ELECTROL. cc	CELL INSIDE VOLUME cc	VOL. INSIDE CELL - (CORR. ELECTROL.) cc	CORE WEIGHT g	CORE WEIGHT VOL. g/cc	% ELECTROL. WEIGHT TO CORE WEIGHT %
	UNIT											
THIN PLATE PRESS	36	1	19/20	397	381	768	50.3	1164	396	2430	6.09	81
BASELINE NEG. ELEC.	64	8	17/18	330	449	779	44.9	1164	385	2399	6.21	19
THIN PLATE PRESS	50	3	19/20	375	362	737	50.9	1164	427	2580	6.06	19
THIN PLATE PRESS	53	3	19/20	373	383	756	49.6	1164	408	2580	6.32	19
THIN PLATE INS AUX.	57	3	19/20	373	364	737	50.9	1164	427	2580	6.04	19
THIN PLATE IN. AUX.	62	3	20/21	394	311	705	55.3	1164	459	2710	6.17	19
THIN PLATE TIGHT	98	3	20/21	394	313	707	55.7	1164	457	2710	5.93	19
BASELINE PRESS	95	3	17/18	408	303	711	57.4	1164	453	2685	5.92	19

$\bar{x}$ = 6.13
STD. DEV. = 0.096

APPARENT CORE DEN. = 6.13 g/cc

FIGURE 78

For the hundred amp hour cell we have 1164 cc. We use the core weight as cw, and of course we have the apparent core volume density of 6.13 grams per cc.

Now, if you use equation one to determine the electrolyte volume you can use this equation. This is a special case. If you go for 50 percent free volume you can go to this equation. We take the core weight and divide by this constant and come up with an electrolyte volume and get a uniform filling.

Could I get back to the first table, please.

(Slide 77.)

We found one thing by going to the original technique, whereby we add the 21 percent electrolyte volume to core weight, we came up with a free volume of 50.4 percent. By this one here by 50.0 which is a higher free volume we had a lower ratio core weight.

So we felt that the core weight technique is not as accurate in determining what the free volume is, and we just used this as a guide, since we have different designs and we cannot reestablish for each design the free volume. So we used this technique, which was in table 2, as a guide to the way of filling the electrolyte volume, based on the free volume, and based on the inside volume of the cell.

Are there any questions on that?

HAINES: Is the performance of your cells as uniform as these figures?

GASTON: Yes.

HALPERT: Any other questions of Steve?

(No response.)

Thank you, Steve.

(Applause.)

HALPERT: Charlie Palandati, of our laboratory, has some interesting results that deals with a silver zinc cell, but actually involves the internal structure of the cell and the combs, and he has some data and some photographs which show what happens to combs when they are subjected to certain g forces.

At this point I will let Charlie talk about the effects on his cell.

PALANDATI: I must confess this morning I felt that I was completely out of place. This evening I feel like I am completely brainwashed. So, during the next several minutes, if I should mistakenly refer to the various electrodes as nickel or cadmium, please don't be too critical.

The discussion is definitely based in regards to silver zinc cells.

A design study for a Venus multiple probe mission was completed at Goddard in 1972. The spacecraft consists of a bus vehicle, a large probe and three small probes. Sealed silver zinc batteries were selected for the mission.

May I make a statement right now, that all ampere hour capacities that will be discussed during this presentation will be based on a manufacturer's nominal ratings. This is for the benefit of the people in the audience that have the actual Goddard design review.

The bus vehicle has a solar array and a battery charger and two 5 ampere hour batteries. The batteries will deliver the electrical power during the launch phase and peak power requirements for midcourse trajectory operations and all probe separations.

The electrical power for the large probe is obtained from a 21 ampere hour battery. Each small probe has a 5 ampere hour battery.

Upon entering the Venus atmosphere parachutes will be released on each probe to reduce the entry velocity. The probes will encounter deceleration forces of 500 g's during the deployment of the drogue chutes.

Review of the environmental parameters for the probes indicated that preliminary tests would be required in order to determine the effects of the high g deceleration forces.

Thirty-five ampere hour and thirty 21 ampere hour cells were purchased for the preliminary tests.

(Slide 80.)

Two methods were used to immobilize the plate stack of the 5 ampere hour cells. Hold-down bars were used

as one method. They consisted of two vertical numbers and a horizontal member. The other method was comprised of putting epoxy on the top of the electrodes and completely covering the wiring that go to the terminal posts.

Both Tom and I felt that better quality control during the manufacturing process could be achieved with the hold-down bars, whereas shifting of the electrodes and separator system during deceleration would probably be less severe with the epoxy method.

The mobilization with epoxy was being studied for high g shock levels on several NASA projects and, therefore, only five cells of each 30 cell lot had epoxy. All the other cells utilized the hold-down bars.

The project office specified that qualification design levels for preliminary tests would have to be at least one-and-a-half times the flight levels, or 750 g's.

(Slide 81.)

The top diagram is the actual flight deceleration profile. The g loads will take place during a six second period.

The test and evaluation equipment at Goddard was not capable of simulating the flight profile.

The test equipment at the Naval Ammunition Depot in Crane, Indiana was capable of simulating the time profile on batteries comprised of three cells.

Batteries were tested to a 550 g level, which was the maximum capability of the centrifuge.

We felt, at Goddard, that we were 50 g's over the flight level, but on the other hand, we were 200° below the design qual level so, therefore, we decided to test to Crane's maximum capability.

The electrical test procedures for the cells were as follows:

The cells were put through three formation cycles and then recharged. At this time the cells were sealed, the three-cell batteries were then accelerated, the cells were discharged and then subjected to two more charge-discharge cycles. The entire cycling regime was performed on individual

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cells, not batteries, all discharges were to one volt.

During the acceleration test the batteries were discharged at a C over 3 rate. Battery current and cell voltages were monitored during acceleration.

Acceleration tests to the 825 g or one-and-a-half times the Crane level were performed at the Naval Research facility at Chesapeake Beach, Maryland. The equipment could not simulate the time profile. The time profile you see in the lower diagram was selected for the test.

The centrifuge was manually controlled and, therefore, the rise and fall times and, also, the g level we were testing to varied for each battery test. The g levels varied from 850 to 965 during the various battery tests.

(Slide 82.)

The batteries are placed in a test fixture designed to prevent vertical and lateral movement of the cells during acceleration. Four 5 ampere hour and 21 ampere hour batteries comprised of cells with hold-down bars were accelerated to 550 g's in one of the following axes:

Plus Y with the g forces going to the edges of the cells.

Plus X with the g forces going in the direction of the broadside of the cells.

Minus Z with the g forces going to the bottom of the cells.

Plus Z with the g forces going towards the terminal post.

The inside edges of two 21 ampere hour cell cases were crazed during the test of the plus Y direction.

The 5 ampere hour and 21 ampere hour batteries with the epoxy plate lock system were erroneously tested in the minus Z direction.

The cells were then discharged and recharged. The electrical performance was normal. The cells were then rechecked. During the recheck one of the 21 ampere hour cell cases ruptured. The 5 ampere hour battery and two remaining 21 ampere hour cells were then subjected to a second 550 g test

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in the plus Z direction. Both 21 ampere hour cell cases ruptured and neither cell was capable of completing the cycling regime.

These two cells were the only cells which failed the electrical test performed at Crane. There were a total of 30 cells tested and of the 30 only two failed the electrical test and they were both 21 ampere hour cells which developed severe rupturing of the cell cases.

Substantial shifting of the electrode stack was observed on all cells with the hold-down bars tested in the plus Z direction.

One or more of the following factors may have caused the 21 ampere hour cell case failures:

(1) The 21 ampere hour cell case walls were thinner than the 5 ampere hour cell case walls.

(2) The batteries had not been properly clamped in the test fixture. Vertical movement was possible during the test.

(3) Several 21 ampere hour cells had swelled during the test regime. When the 21 ampere hour cells were in a fully charged state the electrolyte level was above the top of the plate. When this condition exists internal pressures can develop during cycling, therefore, causing the cells to swell, which would create an additional strain on the cells.

This electrolyte was used in a nine 21 ampere hour cells accelerated at 825 g's. All cell thicknesses remained normal during the entire test so, therefore, I do feel that part of the problem may definitely have been the fact that the cells were flooded.

There was a fourth factor. There was supposed to be a Goddard representative from the Test and Evaluation Division present during the acceleration test at Crane. Due to a lack of travel funds this gentleman was not there.

(Laughter.)

I feel that the second and third factors I just mentioned could have definitely been eliminated. I feel definitely there would have been no reason to accidently test the cells in the wrong direction, and the cells would have definitely been clamped.

re63

Two 2 ampere hour and 21 ampere hour batteries comprised of cells with hold-down bars were acce ted in the plus Y and plus Z axis to the 825 level.

A third battery for each ampere hour size was accelerated in the plus Z direction. These batteries consisted of two cells with epoxy and one cell with hold-down bars. All six batteries successfully completed the 825 g test. There were no cell case failures.

The remaining slides pertain to the 825 g test in the plus Z direction.

(Slide 83.)

These are the 5 ampere hour cells. These are the cells that had the hold-down bars. As you can see there was severe shifting of the electrodes. In fact, actually what you are looking at here is the photographs taken approximately two weeks after the acceleration test and during this period of time the cell stack did shift downward. This phenomena was also evidenced out at Crane during the 500 g test.

This is the cells with the epoxy plate lock system and, as you can see, the difference here is a cell with the hold-down bars and here is the cell with the epoxy. There is shifting, but it is minimized with the epoxy.

(Slide 84.)

What you see here are the internal components of one of the 5 ampere hour cells. These are all the negative electrodes. These are the zinc electrodes.

This is woven nylon and this is cellophane.

This is not the entire separator system, just part of it.

This particular cell here is one with the hold-down bars. As you can see, some of the electrodes were damaged on the top. The zinc plates didn't appear to have any damage. In fact, if one looks at the amount of charged silver on the top it appears that definitely the positive electrodes shifted more than the zinc electrodes.

(Slide 85.)

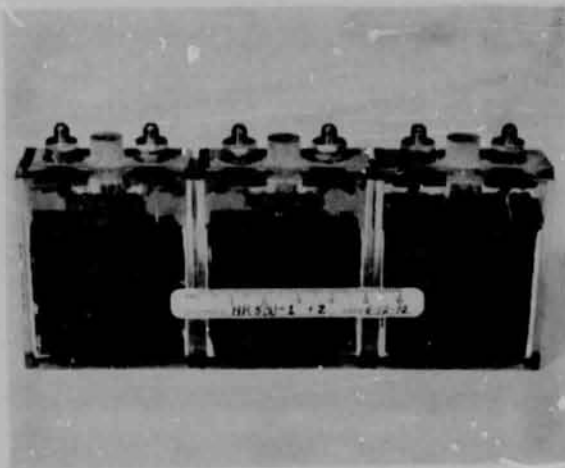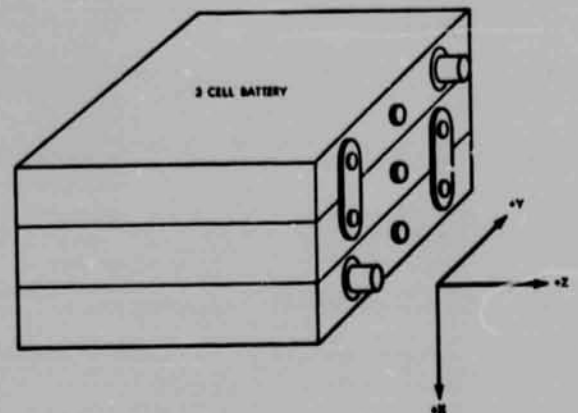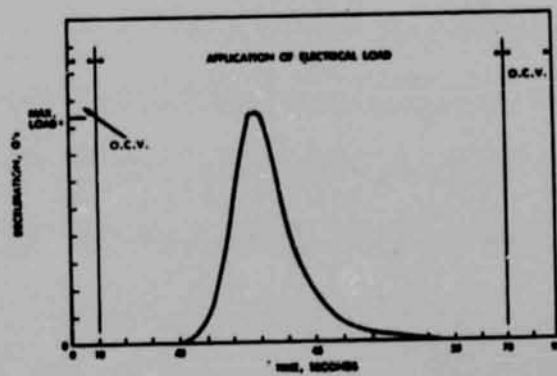This, again, is the internal components of one of

FIGURE 80
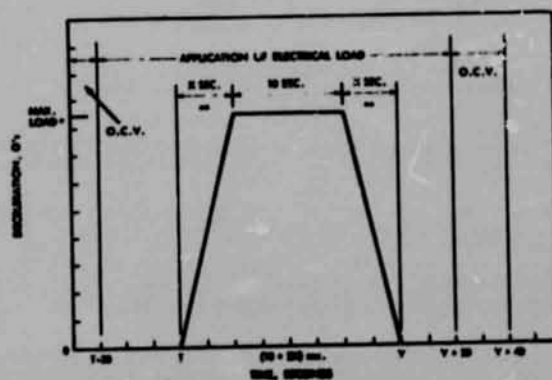

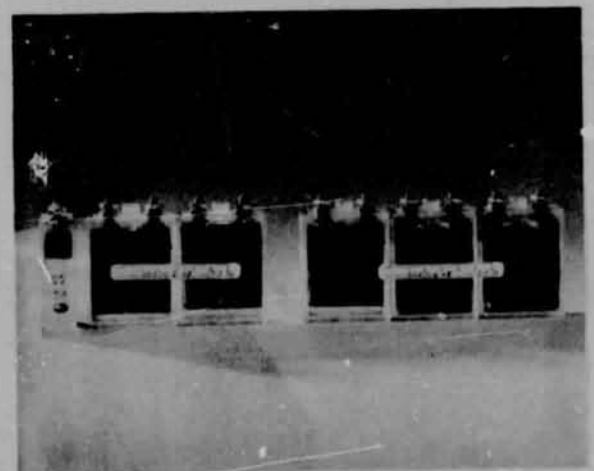**FIGURE 82**

*To be determined

FIGURE 83

FIGURE 81

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the cells with the epoxy. Unfortunately, in trying to separate the epoxy from the plates we end up damaging the separator material and we end up even effecting the plates in several instances, such as right here. This was not done due to the acceleration, this was done in the process of dissecting the cells.

We didn't see any adverse conditions in regards to any of the cells.

(Slide 86.)

This, again, is all the plates for one of the 21 ampere hour cells with the hold-down bars. Here are all the positive electrodes. Again, we have some of the separator system in the photograph. This is woven Pollen, and this again is Pellon here, and this is cellophane.

As you can see, this particular cell, the plates went directly up to the very top of the cell and they were severely damaged.

The zinc plates did not appear, again, to be damaged severly. In fact, there seemed to be little or no evidence of the zinc plates really coming in contact with the hold-down bars.

There was one thing we did observe here, that the grids of the zinc electrodes on the 21 ampere hour cells were weak. This was caused during the welding process of the leads to the grid. There were four leads on each grid and in the process of welding the grids were weakened.

This has been remedied. The grids are now modified on any other cell designs.

The cells that were tested at Crane, there was some slight evidence that they did possibly touch, but that is about all. There was no question about it that the 825 g level severely -- there was a substantial difference in fact. It was much more severe on the 825 g level than the 500 g level.

(Slide 87.)

These, again, are the internal components of one of the 21 ampere hour cells with the epoxy plate lack system. This part. ilar damage you see on the top of the electrodes was done in the process of trying to dissect the cell or remove the epoxy from the edges of the plates.
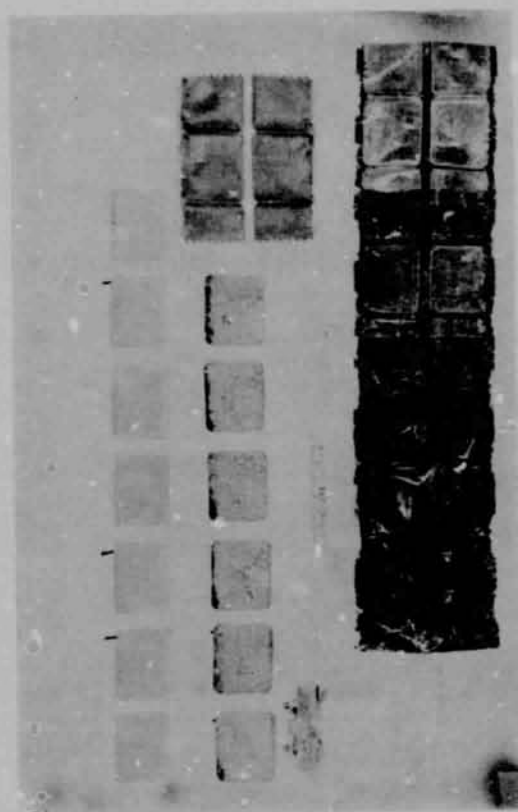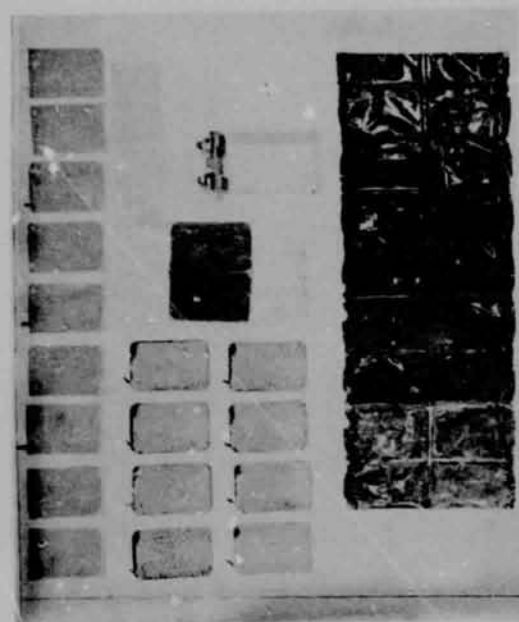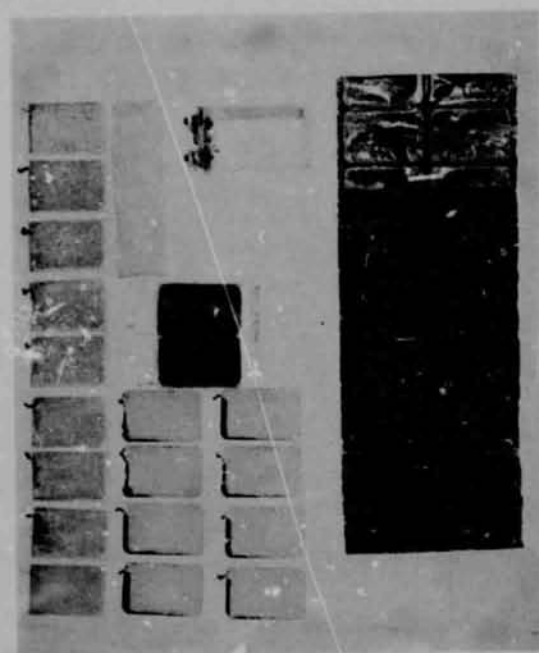
FIGURE 85

FIGURE 87

FIGURE 84

FIGURE 86

134A

We did see hairline cracks though in this area on several electrodes. This is the only damage that we did see, if you want to refer to it as damage. Evidently there was definitely no adverse effect on the electrical test from it.

The zinc plates were all intact. Again, in the process of dissection we tore up a separator system to a slight degree.

(Slide 88.)

One-hundred-twenty-five ampere hour and 21 ampere hour cells with the epoxy plate lock system have been purchased to perform further electrical studies for the Venus mission. The only design modification is in the zinc electroes, and that is, the grids of the zinc electrodes of the al ampere hour cells.

Thank you.

Are there any questions?

STEINHAUER: Charlie, was it considered necessary to the mission to incur the deceleration forces toward the terminals?

PALANDATI: This is something we were looking into, Bob. One of the things was, was there any one particular axis that possibly we would have to avoid. The basic idea here during the preliminary designs was to definitely shoot for going in any direction and not try to put some sort of a restriction on the project office and say, "Look, you can't go in that particular attitude." We definitely were striving to make sure that the cells would be capable of going in any attitude.

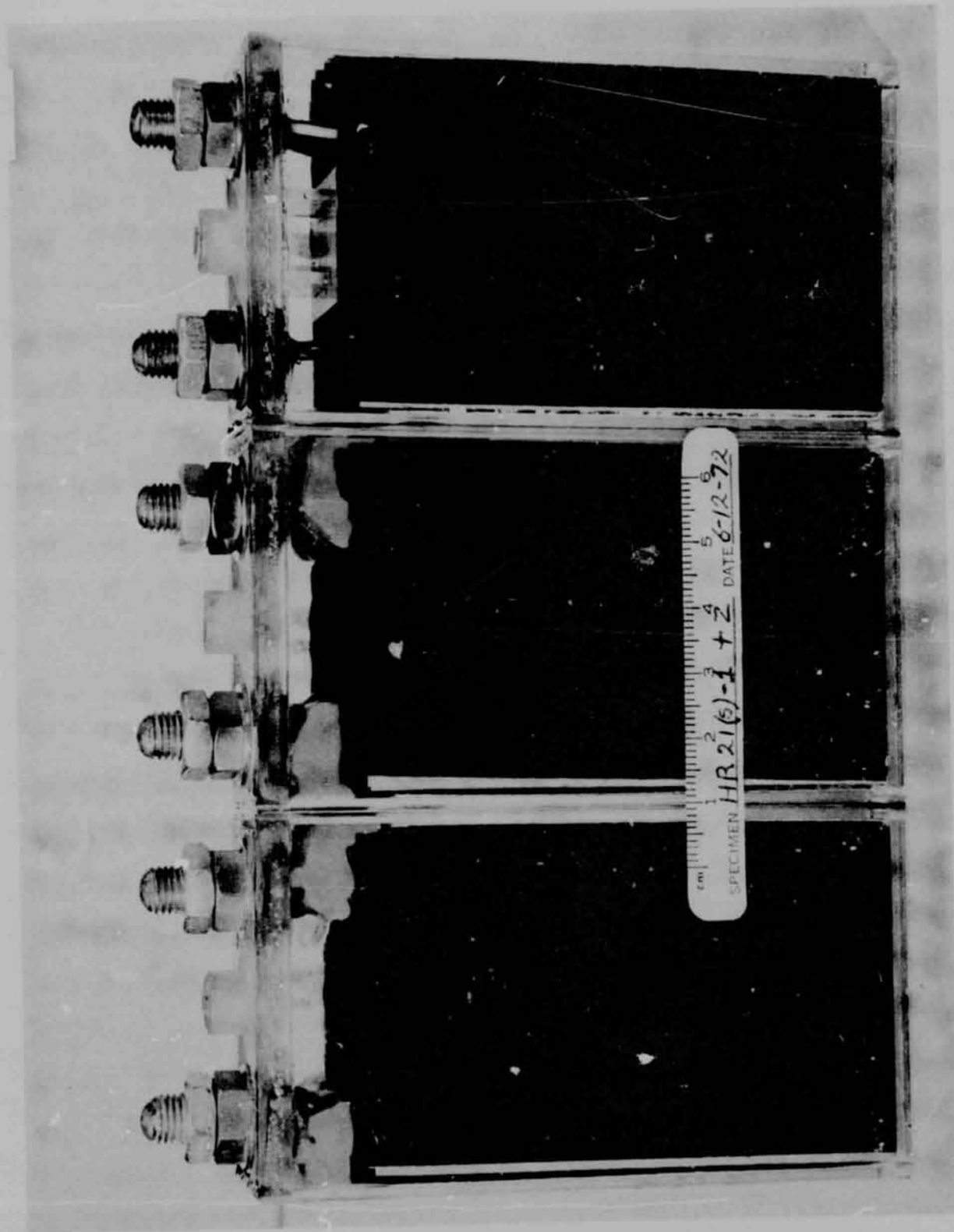GASTON: I have two questions.

First question is: what kind of plastic was the cell case?

PALANDATI: The cell case is a Bakelite C-11.

GASTON: On the positive electrode, what was the grid material? It was an expanded material, I assume.

PALANDATI: Yes, it was a silver Ex-met.

GASTON: Do you know by any chance the number?

NASA G-72 -8160

FIGURE 88

135A

re66

PALANDATI: Yes, I do know the number. Let me put it this way.

Goddard no longer has the Venus mission. At the moment the Ames Research Center has the mission and I have been asked not to give out any of the actual battery specifications. In fact there is a gentleman here from Ames, John Rubenzer. John, would you like to possibly elaborate on this?

RUBENZER: Yes. If you want the information just direct your questions in writing to Ames Research Center in care of the Venus Program. (See Page 6 of second day)

GASTON: No, it was just curiosity.

GROSS: Did you take any measurements, Charlie, during the acceleration testing?

PALANDATI: Measurements in regards to what now?

GROSS: Battery voltage.

PALANDATI: Oh, yes, definitely. All cell voltages were monitored. The battery currents were monitored.

GROSS: How did you do that?

PALANDATI: They had a high speed recorder for one thing. Of course we had voltage leads coming off each cell.

GROSS: The reason I ask that is, because this is a test that we found really important in order to detect small intermittent shorts.

PALANDATI: Yes, this is true.

GROSS: You didn't find any?

PALANDATI: We saw no voltage deviations whatsoever throughout both tests, except for one of the 21 ampere hour cells that the cell case ruptured. In fact on that particular cell, not only did the cell case rupture, the plates buckled. It was the top cell. In fact the plate stack almost looked like the actual g profile we put it through, it went completely up and back down again. That was the only cell where we saw a momentary fluctuation in the voltage and, again, the voltage was still above 1.67 volts.

GROSS: We have run tests similar to that that is standard qualification of silver zinc batteries and found that the weakest orientation was the Z axis.

PALANDATI: Yes. Like I say, there have been several other studies at the high shop levels performed on several NASA projects and, again, this always shows up, it is the plus Z axis. That is the problem.

SULKES: Was there any special reason why those cells were reversed?

PALANDATI: No, it was an accident, this is it. Actually let me put it this way. The battery people at Crane definitely said the plus Z was in the direction we wanted it to be.

SULKES: No, I am not saying physically. I can see by the copper in the separator on the negative end that those cells were electrically reversed, not in the acceleration.

PALANDATI: These cells were reversed?

SULKES: Electrically reversed.

PALANDATI: No.

SULKES: If you will notice on your figures, your pictures, you had layers showing the silver and then a clear layer, and then the layer on the negative showed a darkening and your negatives had this blue cast which comes probably from a copper grid that was in the negative.

PALANDATI: You are talking about the copper oxide. This is a silver grid, this was not a copper grid. These are silver Ex-met on the grid.

SULKES: That is unusual coloring then on the negative separator.

PALANDATI: I think you are referring, more or less, to the primary silver zinc cells where they use the copper sheet?

SULKES: No, it is just on your pictures you show a coloration on the negative end of the separator on your slides, which has to come from either silver or copper attacking that separator.

PALANDATI: Are you talking about the bottom separator now, that I showed?

GROSS: Yes.

PALANDATI: That is the C-19 for the positive plates.

GROSS: Yes, but you go next to the positive as you go from left to right on the negative side. Put one on.

PALANDATI: Yes. Dave, could you, or one of you gentlemen there, put one on? Any one would be fine.

(Slide.)

SULKES: Okay, on your far right. You are showing silver from the other end coming through, but then you should see nothing on your negative end. It shows normally that would either be some silver or copper coming from reversal.

PALADANTI: There was definitely no evidence of reversal on all the electrical data. No cells ever went down below one volt during the discharge. The ampere hour capacities at the end of 6 cycles were 27 ampere hours on all cells, and this was obtained through all 6 cycles.

SULKES: Well, it doesn't necessarily have to reduce the capacity, but it is rather an unusual pattern when you remove the separator to see that, unless it has in fact been electrically reversed.

PALANDATI: I see what you are saying, but offhand I don't have an answer for it.

HENNIGAN: A couple of years ago we ran these same cells in several types of cycling with cellophane 2291, and some other odds and ends, and there was no copper in the cell and they were never reversed, but they call came out blue.

PALANDATI: Right.

HENNIGAN: Now, when you look at the plate when they come out of the cell there is a blue cast to them. I think it shows it up more here.

PALANDATI: That is true, there is a blue cast to some of these zinc electrodes.

HALPERT: Thank you, Charlie.

(Applause.)

(Whereupon, at 5:35 p.m., the workshop was
adjourned, to reconvene on Wednesday, November 15, 1972.)

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